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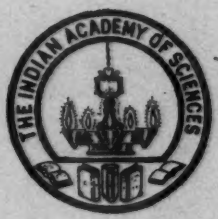

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USE OF MERCURIC ACETATE IN ORGANIC PREPARATIONS—PART I

Mercury Compounds of Amides and Imides

By N. V. Subba Rao and T. R. Seshadri

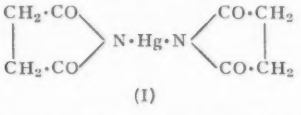
(From the Department of Chemical Technology, Andhra University, Waltair)

Received June 5, 1939

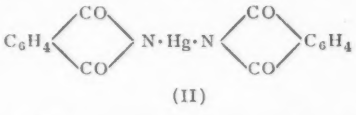
From time immemorial, compounds of mercury have been valued as antiseptics, diuretics and antisyphilitics. Inorganic compounds are easily ionised and absorbed in the system and hence are toxic. Further, compounds like mercuric chloride are caustic due to their capacity to precipitate proteins. There has therefore been a persistent search for suitable organo-mercury compounds which do not give mercury easily in an ionised condition and are not toxic but possess the useful properties above mentioned. As a result, a large number of organo-mercury compounds have been made. According to Kolmer and Raiziss, these compounds can be divided into the following four groups : (1) Simple organic, (2) Pseudo complex organic, (3) Half complex organic and (4) Fully complex organic. (See *Pharmaco Therapeutics* by Cohen and Githens. D. Appleton & Co., Ltd., New York, 1928, p. 657.) The compounds belonging to class 1 (*e.g.*, mercury salicylate) ionise more or less completely in water and hence have strong bactericidal action but they are also toxic. Compounds coming under classes 2 and 3 (*e.g.*, mercury succinimide, flumerin, mercuro-chrome, etc.) ionise less readily or do not ionise at all and the presence of mercury can be detected only by means of ammonium sulphide. The minimum of toxic properties is found in these two groups and at the same time the antipathogenic action is fully available. In the last group of compounds (*e.g.*, metaphen), mercury is so firmly bound that it cannot be removed or split off even by boiling with water and ammonium sulphide. Hence they are very slow in their action.

The mercury compound of succinimide (I) which is said to have been employed with good results in cases of syphilis and pulmonary tuberculosis has been prepared till now by the action of mercuric oxide on succinimide in aqueous or alcoholic solution[1] or by the action of mercuric chloride on the potassium derivative of succinimide.[1] The same methods have been used for obtaining the mercury derivative of phthalimide[1] (II). It is now found that the preparations can be made far more conveniently by mixing an

alcoholic solution of the respective imide with a similar solution of mercuric acetate. The reaction is quick and the yield and purity of the product very high. It has been observed that even with a large excess of mercuric acetate, the same di-imido mercuri compounds are produced and no other products are formed. Mercury phthalimide is more sparingly soluble in water than the succinimide compound and hence may be preferred where greater retention of mercury in the body and slower action are desired.

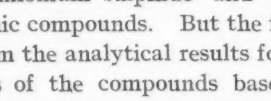


(I)

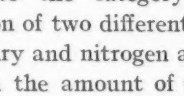


(II)

Liebig[2] (1853) noted the formation of a compound of urea with mercuric oxide having the formula CON_2H_4, 2 HgO. With mercuric nitrate and urea, he obtained a product of the composition 2 CO $(NH_2)_2$, Hg $(NO_3)_2$, 3 HgO. Ruspaggiari[3] (1897) reported the preparation of compounds containing the divalent group $CO\langle^{NH\cdot Hg'}_{NH\cdot Hg'}$, and using mercuric acetate, he isolated a compound having the formula of di-acetoxymercuri urea (III). It has now been found that urea reacts readily with mercuric acetate in aqueous or alcoholic solutions to give rise to two different compounds depending on the proportion of mercuric acetate employed. Using one molecule of mercuric acetate for each molecule of urea, a colourless micro-crystalline compound melting above 340° C. and having a formula (IV) is obtained. Using two molecular proportions of mercuric acetate or excess, a second compound having the formula (III) as suggested by Ruspaggiari[3] could be isolated. Both the compounds are similar in their solubilities and reactions towards alkali and ammonium sulphide and belong to the category of pseudo-complex organic compounds. But the formation of two different compounds is evident from the analytical results for mercury and nitrogen and from the relative yields of the compounds based upon the amount of urea used as starting material. The compound IV can be used with advantage in place of mercury succinimide as it has very similar properties, as the raw material, urea is very cheap and as the compound has a high mercury content.



(III)



(IV)

$CH_3\cdot CO\cdot NH\cdot Hg\cdot O\cdot CO\cdot CH_3$

(VI)

$(CH_3\cdot CO\cdot NH)_2\,Hg$

(V)

In the formation of these compounds, urea obviously behaves like a diamide in which a hydrogen atom of each amide group is capable of being replaced by mercury. It is well known that acetamide reacts with mercuric oxide when heated at 180° C. to give rise to mercury acetamide[4] (diacetamido mercury) (V). When mercuric acetate is used in the place of mercuric oxide in the above reaction and heated for 1 hour a very complex change takes place. The clear liquid mixture that is first produced rapidly evolved acetic acid and as a result of further decomposition globules of mercury began to collect and the whole mass solidified. From the product no pure compound could be isolated. For the preparation of mercury acetamide (V), the use of mercuric oxide is therefore the most convenient.

When two molecules of acetamide are allowed to react with one molecule of mercuric acetate in alcoholic solution, a colourless crystalline compound resembling mercury acetamide in most of its properties is obtained. But on detailed analysis, it is found to be different and to have the formula of acetoxymercuri acetamide (VI).

When larger quantities of mercuric acetate are employed, a colourless crystalline compound melting at 225° C. and containing 72·0 per cent. mercury and 3·9 per cent. nitrogen is formed. No definite composition could be given to this substance and it is still under investigation.

Experimental

In preparing solutions of mercuric acetate in water or in alcohol a few drops of acetic acid were always added in order to render them clear.

Mercury succinimide (*I*).—When to a clear solution of succinimide (2 g.) in alcohol (15 c.c.) was added a similar solution of mercuric acetate (3·3 g.) in alcohol (60 c.c.) a colourless crystalline solid separated immediately. It was filtered, washed with a little alcohol and air dried. The yield was 3 g. (nearly 75 per cent.). The substance appeared as rectangular rods under the microscope and melted at 262° C. with decomposition. It was readily soluble in cold water and the solution did not precipitate mercuric oxide on the addition of alkali. It however formed mercuric sulphide when treated with ammonium sulphide solution. (Found: Hg, 50·3; $C_8H_8O_4N_2Hg$ requires Hg, 50·5 per cent.)

In the above preparation, succinimide and mercuric acetate were used in the proportion 2 : 1. Using double the above quantity of mercuric acetate (1 : 1) did not produce any change in the yield or the nature of the product.

Mercury phthalimide (*II*).—When a clear solution of phthalimide (2 g.) in hot alcohol (25 c.c.) was added to a cold solution of mercuric acetate

(2·2 g.) in alcohol (40 c.c.), a colourless crystalline compound (needles) separated immediately on stirring. The precipitate was allowed to settle, filtered, washed with a little alcohol and dried in air. The yield was 3·2 g. (nearly quantitative). The substance did not melt below 300° C., was insoluble in cold water but dissolved to some extent in hot water. In other respects it resembled mercury succinimide closely. (Found : Hg, 39·8; $C_{16}H_8O_4N_2Hg$ requires Hg 40·6 per cent.) Using excess of mercuric acetate did not introduce any change.

Mercury carbamide (*IV*).—To a cold solution of urea (1 g.) in water (10 c.c.) a solution of mercuric acetate (6 g.) in water (40 c.c.) was added. (In preparing the clear solution of mercuric acetate, the minimum of acetic acid should be used as otherwise the yield of the product would be considerably diminished.) There was immediate precipitation of a colourless crystalline solid and the reaction was complete in a few minutes. The solid was filtered, washed with a little water and dried in air. The yield was 3·2 g. and the substance appeared as small crystalline plates under the microscope. On heating it turned yellow at 230° C. and decomposed at 340°–345° C. It was sparingly soluble in cold water but dissolved appreciably in boiling water. (Found : Hg, 76·8 ; C, 4·9 ; N, 11·0 ; CH_2ON_2Hg requires Hg, 77·6 ; C, 4·6 ; N, 10·8 per cent.) The compound was not decomposed by alkalies but ammonium sulphide precipitated mercuric sulphide. It was readily decomposed by acids including acetic acid and hence the need for avoiding excess of this during the course of preparation.

The above reaction could be carried out in methyl alcoholic solution also, though a large volume of alcohol had to be employed owing to the comparatively lower solubility of mercuric acetate in this solvent. The yield was however better (3·8 g.).

Di-acetoxymercuri carbamide (*III*).—A cold solution of urea (1 g.) in water about (10 c.c.) was added to a clear aqueous solution of mercuric acetate (15 g.) in water (80 c.c.). On stirring a colourless crystalline solid rapidly separated. It was allowed to settle, filtered, washed with water and dried in air. The yield of the dry substance was 6 g. It appeared as rectangular plates and prisms under the microscope and on heating decomposed at about 270° C. It was sparingly soluble in water and alcohol in the cold and dissolved to some extent in hot water. In this and most other respects it resembled mercury carbamide. (Found : Hg, 70·2 ; N, 5·2 ; $C_5H_8O_5N_2Hg_2$ requires Hg, 69·4 ; N, 4·9 per cent.) Using a large excess of mercuric acetate (30 g.) did not produce any change in the yield or the composition of the product.

Acetoxymercuri acetamide (*VI*).—When a clear solution of acetamide (1 g.) in alcohol (about 10 c.c.) was added to a similar solution of mercuric acetate (3·5 g.) in alcohol (60 c.c.) a colourless crystalline solid began to separate gradually on stirring. After leaving overnight, the precipitate was filtered, washed and air-dried. The yield was 1·2 g. The substance appeared as long narrow rectangular plates under the microscope and melted at 195° with decomposition. It could be easily recrystallised from alcohol and was readily soluble in water. In its properties it behaved like pseudo-complex organic compounds. (Found : Hg, 63·1 ; N, 4·8 ; $C_4H_7O_3NHg$ requires Hg, 63·1 ; N, 4·4 per cent.)

In the above experiment two molecular proportions of acetamide were employed for one of mercuric acetate. When it was repeated using 7 g. of mercuric acetate (1 : 1) dissolved in alcohol (about 120 c.c.) and the precipitate was collected just as before, it looked pure and crystalline (rectangular prisms) and the yield was found to be almost double. It resembled the above acetoxymercuri acetamide very closely in its properties but it melted with decomposition at 225° C. and was found to have a different composition. (Found : Hg, 72·0 ; N, 3·9 per cent.)

Summary

Mercury compounds of succinimide and pthalimide have been obtained easily and in a pure condition by treating the respective imides with mercuric acetate in alcoholic solution. Carbamide (urea) forms two compounds when it reacts with mercuric acetate in different proportions : (1) Mercury carbamide and (2) Di-acetoxymercuri carbamide. The preparation of mercury acetamide is best effected only through the use of mercuric oxide. When mercuric acetate in alcoholic solution is employed, acetoxymercuri acetamide is formed.

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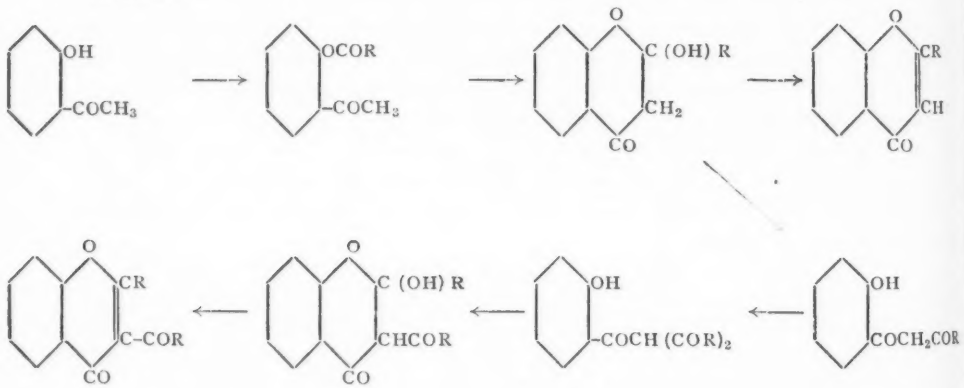
3-BENZOYL-7-HYDROXYFLAVONE

By S. Rangaswami and T. R. Seshadri
(From the Department of Chemistry, Andhra University, Waltair)

Received June 5, 1939

The formation of 3-acetylchromones when an *ortho*-hydroxy-acetophenone is heated with acetic anhydride and sodium acetate is of common occurrence and several 3-acetyl derivatives have been isolated and described.[1] The corresponding series of 3-benzoylflavones when Allan and Robinson's method is employed is not so well known probably due to the ease with which the 3-benzoyl group gets eliminated during the treatment with alkali. Starting from res-diacetophenone Algar *et al*[2] obtained 3 : 3'-dibenzoyldiflavone. During the course of a detailed study of the mechanism of 3-acylation Baker[3] obtained a mixture of 7-benzoyloxyflavone and 7-benzoyloxy-3-benzoylflavone by heating resacetophenone with sodium benzoate and benzoic anhydride. He postulated the following general mechanism for such reactions.



Employing 2 : 6-dihydroxyacetophenone Sugasawa[4] was able to isolate 3-benzoyl-5-hydroxyflavone and he expressed the opinion that a higher temperature than the one ordinarily employed for the condensation is essential for effecting 3-benzoylation.

While repeating the preparation of 7-hydroxyflavone by the procedure adopted by Robinson and Venkataraman[5] it was frequently found by us that

the product after hydrolysis was very sparingly soluble in alcohol and acetic acid from which 7-hydroxyflavone can be conveniently crystallised. By careful fractionation it could be easily separated into two components, the more soluble one being 7-hydroxyflavone. The less soluble fraction which could be crystallised from pyridine melted at 264–65° and had the composition $C_{22}H_{14}O_4$. On further hydrolysis by boiling with aqueous sodium carbonate it gave rise to benzoic acid and 7-hydroxyflavone. It could readily be distinguished from its isomer, 7-benzoyloxyflavone because it had a much higher melting point, dissolved readily in cold dilute alkali and formed an acetyl derivative. It is therefore given the constitution of 3-benzoyl-7-hydroxyflavone.

Our experience shows that 3-benzoylation takes place to a very high degree under the ordinary conditions of the synthesis of the flavones. Using the difference in the ease with which the benzoyloxy and the C-benzoyl groups undergo hydrolysis, by suitable modification of the treatment with alkali it is possible to obtain either the free hydroxyflavones, or their 3-benzoyl derivatives. In some experiments as high as 80 per cent. of the product was found to be 3-benzoyl-7-hydroxyflavone. It should however be noted that the same conditions do not work satisfactorily in all cases, since using phloracetophenone we could obtain only chrysin and failed to isolate the corresponding 3-benzoyl compound.

Experimental

3-*Benzoyl-7-hydroxyflavone.*—An intimate mixture of resacetophenone (10 g.), sodium benzoate (12 g.) and benzoic anhydride (40 g.) was heated for 4–5 hours in an oil-bath at 180–190°. The residue was then boiled with 10 per cent. alcoholic potash (250 c.c.) until complete solution was effected (about 20 min.) Most of the alcohol was then distilled off (15–20 min.), the residual liquid diluted with water and saturated with carbon dioxide. The precipitate obtained was filtered, washed with water and then boiled with a large volume of glacial acetic acid. The portion insoluble in acetic acid was crystallised from pyridine in which it was moderately soluble whereby the 3-benzoyl compound was obtained as narrow rectangular rods and prisms melting at 264–65.° (Found : C, 77·5 ; H, 4·1 ; $C_{22}H_{14}O_4$ requires C, 77·2 ; H, 4·1 per cent.)

The compound dissolved readily in cold dilute sodium hydroxide giving a pale yellow solution from which it was re-precipitated by acids. The yellow solution in concentrated sulphuric acid exhibited no marked fluorescence and a solution in alcohol showed no ferric chloride colouration. The acetate prepared by the action of boiling acetic anhydride and fused sodium acetate

crystallised from an alcohol-acetic acid mixture as rectangular prisms and tablets melting at 192–94°. (Found : C, 75·0 ; H, 4·5 ; $C_{24}H_{16}O_5$ requires C, 75·0 ; H, 4·2 per cent.)

Hydrolysis to 7-hydroxyflavone.—The above compound (1 g.) was boiled with 5 per cent. aqueous sodium carbonate (40 c.c.). The substance went into solution within the first 10 minutes. After boiling for 2 hours the resulting solution was cooled and acidified when a precipitate was formed. This was filtered and boiled with a little water and filtered hot. Subsequent crystallisation from alcohol yielded colourless rectangular prisms of 7-hydroxyflavone melting at 244–45°. From the mixed aqueous filtrates benzoic acid was obtained by ether-extraction.

Summary

3-Benzoyl-7-hydroxyflavone has been prepared and its properties have been studied.

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THE BRIGHT SOLAR ERUPTION OF MARCH 3, 1939

By M. Salaruddin and C. K. Ananthasubrahmanyam
(From the Kodaikanal Observatory)

Received May 8, 1939
(Communicated by Dr. A. L. Narayan, D.Sc., F.Inst.P.)

In recent years a number of papers have appeared on bright chromospheric eruptions and their association with ionospheric and terrestrial magnetic disturbances. There seems to be fairly good evidence that the correlation between these is closest for the brightest and most extensive solar eruptions. From the nature of the several terrestrial effects it would appear that they are caused by a sudden increase in ionisation in some portion of the ionosphere. The purpose of this note is to describe one of these solar fireworks observed recently at the Kodaikanal Observatory. This was the brightest and the largest eruption that has been observed here during these two years, its intensity at maximum being four times that of the undisturbed disc with its total area amounting to about 500 millionths of the sun's hemisphere, (600 million square miles nearly).

The eruption was observed on March 3, 1939, and a series of 43 spectroheliograms were obtained at intervals of about one minute showing the successive appearances of this eruption in Hα light, with a simultaneous observation of the phenomenon in the Hale Spectrohelioscope.

There was no trace of the eruption in the spectroheliogram taken at 7^h–58^m I.S.T. and no special activity was seen in the spectrohelioscope observations till about 8^h–20^m when suddenly the area just to the south of the spot-group Kodaikanal No. 6976 was noticed to become eruptive. The spot-group was then 25° to the west of the central meridian and at latitude 18° S. This group was first seen on February 23rd as a single spot of regular outline at 72° east of the central meridian. It continued as a single spot till February 28 when it was showing signs of breaking up. When it was again observed on March 1, it had already broken up into two and the components got separated from each other by about 2° forming a bipolar group. It remained as a bipolar group till the time of the eruption on March 3, after which the preceding spot got split up into a number of smaller ones, the whole group passing out of the visible disc at the west limb on March 7.

As observed at the spectrohelioscope, a small area close to the preceding spot in the group brightened up suddenly at 8^h–20^m and this area quickly extended in a narrow streak ending in a bright knot. The whole streak now assumed a hook-like shape and increased rapidly in brightness attaining the maximum intensity of 4 times that of the undisturbed disc at 8^h–30^m.[1] The intensity then began to decrease gradually and was three times that of the undisturbed disc at 8^h–50^m. The brightness was reduced to that of a normal flocculus at 9^h–05^m. Thus it is seen that the eruption began at 8^h–20^m, attained its maximum brightness at 8^h–30^m and subsided at 9^h–05^m.

In the accompanying Plate I, spectroheliogram 1 taken at 7^h–58^m shows the spot-group region before the commencement of the eruption. In No. 2 taken at 8^h–22^m the eruption had already begun and we see it extending towards the nucleus. The spectroheliograms 3–23 were taken between 8^h–40^m and 9^h–13^m at intervals of less than a minute. The eruption had already attained its maximum brightness before spectroheliogram No. 3 was taken and the succeeding plates of the series show it decreasing in brightness. The rapid decrease in intensity is clearly seen in the spectroheliograms 10–16 taken between 8^h–50^m and 8^h–54^m. An interesting feature that can be readily seen from a reference to the plate is that the flocculus retained its general shape throughout the eruption, while the relative intensities varied at different points. In the beginning, the part of the flocculus nearer the spot was brightest and then the brightness gradually shifted to the nucleus at the other end of the flocculus suggesting clearly that the eruptive matter had been flowing from the spot to the nucleus. No marked Doppler shift was observed in any part of the flocculus during the eruption.

From 9^h–05^m to 10^h–00^m no special activity was noticed in the region of the spot-group, excepting a faint dark-marking to the west of the group which showed a displacement of 0·6 Å to red at 9^h–50^m. But at 10^h–00^m, the flocculus to the north of the spot-group suddenly became eruptive attaining its maximum brightness at 10^h–10^m and fading away to its original brightness at 11^h–00^m. The series 24–43 in Plate II show the successive appearance of this eruption between 10^h–13^m and 10^h–35^m. It will be seen that this eruption was in two distinct areas close to each other. The one to the north could be seen faintly connected with the bright nucleus of the previous eruption, whereas the one to the south was in contact with the following member of the spot-group, suggesting that the matter which had

[1] Intensity measurements were made by using a calibrated step-wedge by holding the wedge between the observing eye-piece and the slit of the spectrohelioscope.

flown into the nucleus from the preceding spot in the group during the previous eruption was flowing back into the following spot in the group. Newton and Barton state that a chromospheric eruption does not affect the structure of the spots in the neighbourhood. But in this case we observe that after the eruption, the preceding spot was broken up into several minute spots and the following spot became prominent. Perhaps the bipolar group has again combined to form a single spot and the eruption might have been a preliminary to this transformation.

Mention should also be made of a prominent dark-marking at latitude 40° which was seen connecting the spot-group on March 2, but on the day of the eruption the connecting filaments were not visible. This dark-marking is indicated by means of an arrow in No. 1 of the series in the accompanying plate. On March 8, the prominence given rise to by this Hα absorption marking was seen connected up with the prominence from the spot in question, showing that there had still been some invisible connection between the marking and the spot.

As has already been stated, a close relationship has been found by many observers between bright chromospheric eruptions, ionospheric and terrestrial magnetic effects. The ionospheric and the concomitant terrestrial magnetic disturbances are the only means of detecting the causative radiation. From the nature of these effects, it seems clear that the solar eruption which emits enhanced visible radiation also releases ultra-violet light and that these effects are caused by a sudden increase in ionisation in some part of the ionosphere. Further, spectroheliograms taken over a narrow range indicate little or no increase in the black-body radiation accompanying the eruption. It is believed that these eruptions are evidence of some deep seated disturbance which may manifest itself at widely separated points on the sun. While the larger and brighter eruptions are accompanied by sudden perturbations in ionospheric and magnetic effects, many have been observed which were not associated with radio fade-outs or magnetic changes. The records of the Bombay Magnetic Observatory show that there had been no significant magnetic disturbance on the morning of March 3 and no information is available as to whether there was any ionospheric disturbance at the time.

We wish to acknowledge our gratitude to Dr. A. L. Narayan, the Director of the Kodaikanal Observatory, for assistance in obtaining a rapid succession of spectroheliograms and consideration of results.

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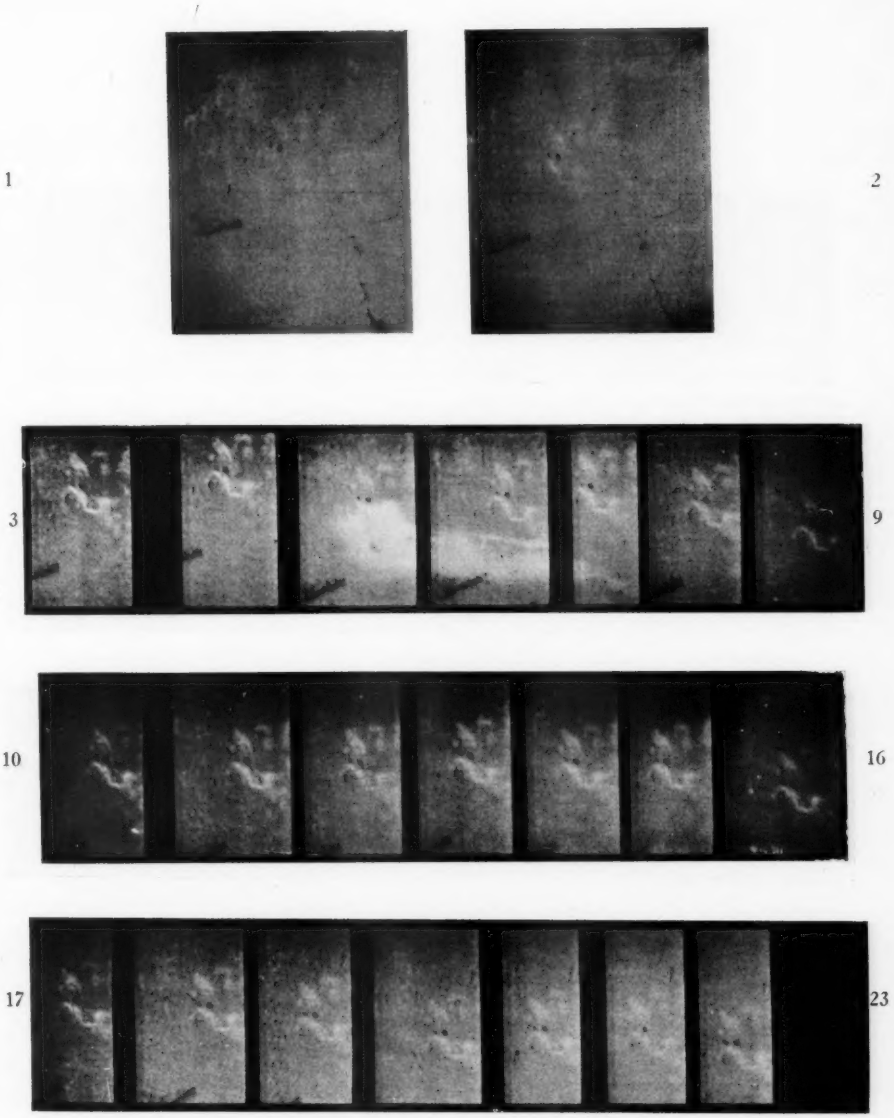
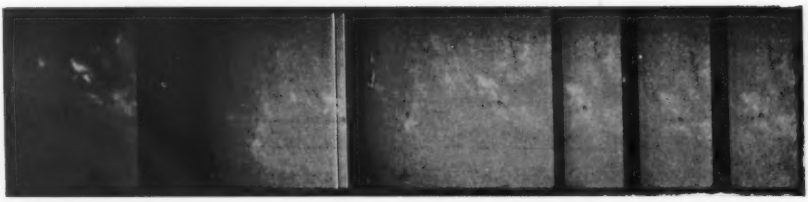
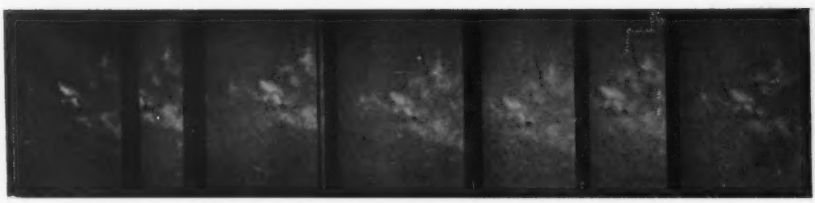
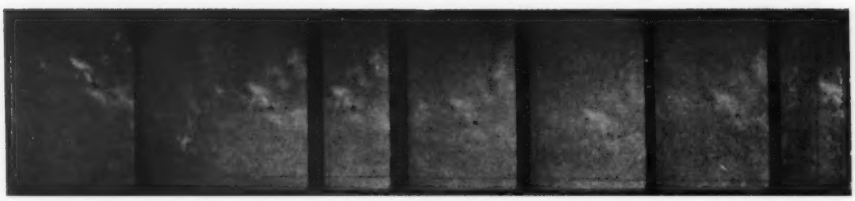


Solar eruption of March 3, 1939







Solar eruption of March 3, 1939

ON NORMAL NUMBERS

By S. S. Pillai

(From the Department of Mathematics, Annamalai University)

Received May 30, 1939

(Communicated by Dr. S. Chowla)

§ I

Let $m(b)$ denote the number of times that the digit b occurs in the first m places when x is expressed in the scale of r. If $m(b)/m \to 1/r$ for every $b < r$, then x is said to be *simply normal* in the scale of r. If x is simply normal in all of the scales $r, r^2, r^3, \cdots$ then x is said to be *normal* in the scale of r.[1] The number $\cdot 1\,2\,3\,4\,5\,6\,7\,8\,9\,10\,11\,12\cdots$ formed by writing down all the positive integers in order, in decimal notation, is proved to be normal by Champernowne.[2] Hardy and Wright say 'The proof that this is so is more troublesome than might be expected'. The object of this note is to give an easy proof for this result and consider some generalisations.

§ II

Unless otherwise mentioned, in this section, the numbers are assumed to be expressed in the scale of r; and 'numbers' means positive integers.

$F(N)$ denotes the total number of digits in all the numbers $\leqslant N$; $K(N)$ denotes the total number of times that the digit b occurs in all the numbers $\leqslant N$, where $b < r$; and $K_t(N)$ denotes the total number of numbers which contain b in the tth place (from the right) and which do not exceed N.

$$n = [\log N/\log r].$$

Lemma 1.—$F(N) = n \cdot N + O(N)$.

If $r^{t-1} \leqslant x < r^t$, x contains t digits. So

$$\begin{aligned} F(N) &= F(N) - F(r^n) + F(r^n) - F(r^{n-1}) + F(r^{n-1}) - F(r^{n-2}) + \cdots\cdots \\ &= (n+1)(N - r^n) + n(r^n - r^{n-1}) + (n-1)(r^{n-1} - r^{n-2}) + \cdots\cdots \\ &= (n+1)N - (r^n + r^{n-1} + r^{n-2} + \cdots) = n \cdot N + O(N). \end{aligned}$$

Lemma 2.—$K(N) = nN/r + O(N)$.

x will contain b in the tth place if and only if

$$s \cdot r^t + b \cdot r^{t-1} \leqslant x < s \cdot r^t + (b+1) \cdot r^{t-1}.$$

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[1] In their *Introduction to the Theory of Numbers*, Hardy and Wright give a slightly different definition which seems to contain superfluous conditions.

[2] *The Journal of London Math. Soc.*, 1933, **8**, 254–60.

Now, the length of the above interval is r^{t-1} and the total number of such intervals in $(0, N) = N/r^t + O(1)$. So

$$K_t(N) = r^{t-1}\{N/r^t + O(1)\} = N/r + O(r^{t-1}).$$

Hence

$$K(N) = \sum_{1 \leqslant t \leqslant n+1} K_t(N) = \Sigma N/r + \Sigma O(r^{t-1}) = n \cdot N/r + O(N).$$

Lemma 3.—When $x = \cdot 1\,2\,3\,4 \cdots$ in the scale of r,

$$m(b)/m \to 1/r.$$

Given m, we can choose N so that

$$F(N) \leqslant m < F(N+1).$$

Since the number of digits in N is $(\log N/\log r) + 1$, we get, from the above, that

$$m = F(n) + O(\log N)$$

and

$$m(b) = K(N) + O(\log N).$$

From this and lemmas (1), (2), the present one follows.

THEOREM I.—$\cdot 1\,2\,3\,4 \cdots$ *is normal in the scale of* 10.

By putting $r = 10, 10^2, 10^3, \cdots$, in lemma (3), we get the theorem.

Let $S(x)$ denote the number of numbers $\leqslant x$, which belong to a given class (A). If $S(x) = o(x)$, the total number of digits in all the numbers of the set $\leqslant x$ is $0(x \log x)$. But by lemma 2, $K(x) \backsim x \log x/(r \log r)$. So we get

THEOREM II.—If $S(x) = o(x)$, then the number $\cdot b_1 b_2 b_3 \cdots$ is normal, where $b_1, b_2, b_3, \cdots$ are the numbers in order not belonging to the set (A).

THEOREM III.—$\cdot 4\,6\,8\,9\,10\,12 \cdots$ is normal, where 4, 6, 8, $\cdots$ are the composite numbers in order.

This theorem of Chapernowne is only a particular case of Theorem II.

§ III

Let $f(x)$ be any function of x; $c_n = [f(n)]$; $G = \cdot c_1 c_2 c_3 \cdots$;

$H(N)$ = the total number of digits in all the $c_s \leqslant N$; and $j(N)$ = the total number of times that the digit b occurs in all the $c_s \leqslant N$.

If $f(x) = x^\alpha$ and $a = 1/\alpha$, as before, it can be easily proved that $H(N) = n \cdot N^a + O(N^a)$; and $j(N) = n \cdot N^a/r + O(N^a) + O(N)$. Hence we get

THEOREM IV.—*If* $f(x) = x^\alpha$ *and* $\alpha \leqslant 1$, *then* G *is normal.*

The above method can be refined to prove

THEOREM V.—*When* $x^\alpha g(x) = X$, *let there be a* $\psi(x)$ *such that* (1) $x^\alpha \backsim X/\psi(X)$, (2) $\psi'(X) = 0\{\psi(X)/X\}$. *Then if* $f(x) = x^\alpha g(x)$ *and* $\alpha \leqslant 1$, *then* G *is normal.*

It may be noted that $\log x$, $(\log x)^{10}$, $\log \log x$, $\log x \times \log \log x$, etc., are suitable values for $g(x)$.

As in Theorem II, even when we remove from $c_1, c_2, c_3, \cdots$, a class whose order is $0(x)$, the resulting G in Theorems III, V will remain normal.

Let $k = 10^{t-1} + 10^{t-2} + \cdots + 10 + 1$; $r = 10$; $b = 1$; and $f(x) = \log x$. Then $H(k) \backsim t \cdot e^k$, and $j(k) \geqslant t(e^k - e^{k-1}) = t \cdot e^k (1 - 1/e)$. So we get

THEOREM VI.—*If* f (x) = *log* x, *G is not normal. If* f (x) = 10^x *it is obvious that G is not normal.*

It is highly probable that G is normal when $f(x) = x^a$ for all a ; in particular, the number $\cdot 1\ 4\ 9\ 16\ 25\ 3649 \cdots$ is normal. But I have no proof.

Can we guess that when $\log f(x)$ is not of the order $\log x$, G is not normal ?

I wonder whether G is normal when $f(x) = 2^x$.

EIN VERSUCH DER ERWEITERUNG DES KRISHNAN'—SCHEN REZIPROZITÄTSGESETZ ESFÜR SCHIEFE BEOBACHTUNGSEBENEN

VON V. S. VRKLJAN *in Zagreb*

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1. Einleitung

R. S. KRISHNAN hat bekanntlich[1] vor etwa vier Jahren ein Gesetz der Kolloid-Optik entdeckt — das sogenannte Reziprozitätsgesetz— dessen Ausdruck in einer einfachen algebraischen Gleichung

$$\rho_u = \frac{1 + \frac{1}{\rho_h}}{1 + \frac{1}{\rho_v}} \qquad (1)$$

ausgedrückt werden kann. Hier bedeutet ρ_u den Depolarisationsgrad des zerstreuten Lichtes (welches in der horizontalen Ebene beobachtet wird[2]), wenn der einfallende horizontale Lichtbündel unpolarisiert wird, ρ_h und ρ_v die Depolarisationsgrade des in der horizontalen Ebene beobachteten zerstreuten Lichtes, wenn der einfallende horizontale Lichtbündel polarisiert wird ; die Indexe h und v bei ρ bedeuten dabei, dass bei den erwähnten Polarisationen der Vektor der elektrischen Feldstärke im einfallenden polarisierten Lichtbündel horizontal bzw. vertikal ist.

Unlängst habe ich in einer Abhandlung[3] die Frage behandelt, welche Form des Reziprozitätsgesetzes für schiefe Beobachtungsebenen auf Grund der Mie-schen Theorie zu erwarten wäre. Hier wird diese Frage von neuen aufgestellt, und zwar in der Richtung, welcher Ausdruck für ρ_u als eine Erweiterung der Krishnan'schen Relation (1) für schiefe Beobachtungsebenen sich ergeben wird ohne Rücksicht auf irgendwelche Zerstreuungstheorie zum Schluss werden dann noch einige Bemerkungen auf Grund der Mieschen Theorie beigefügt.

2. Über die Erweiterung des Reziprozitätsgesetzes für schiefe Beobachtungsebenen und ihre experimentelle Prüfung

Wenn wir die Intensitäte derjenigen Komponenten des zerstreuten Lichtes, deren Vektor der elektrischen Feldstärke in die schiefen Beobachtungsebenen fällt, mit P_h bzw. P_v bezeichnen, je nachdem, ob der elektri-

sche Vektor des einfallenden Lichtbündels in der horizontalen oder der vertikalen Ebene liegt, und weiter die Intensitäte derjenigen Komponenten des zerstreuten Lichtes, deren Vektor der elektrischen Feldstärke normal auf der schiefen Beobachtungsebene steht, mit N_h bzw. N_v bezeichnen, wo die Indexe h und v dasselbe, wie im vorigen Falle (*d. h.* bei P_h bzw. P_v) bedeuten, so ergibt sich als eine sinnvolle Erweiterung der Krishnan'schen Definitionen von ρ_u, ρ_h und ρ_v

$$\rho_u = \frac{P_v + P_h}{N_h + N_v}, \tag{2}$$

$$\rho_h = \frac{N_h}{P_h}, \qquad \rho_v = \frac{P_v}{N_v}. \tag{3}$$

Diese Definitionen sind so ausgewählt, dass sie für den Fall der horizontalen Beobachtungsebene in die bekannten Krishnan'schen Definitionen übergehen.*

Aus der Gleichtung (2) kann man unter Berücksichtigung von (3) gleich ableiten

$$\rho_u = \frac{P_v}{N_h} \cdot \frac{1 + \frac{N_h}{P_v} \cdot \frac{1}{\rho_h}}{1 + \frac{P_v}{N_h} \cdot \frac{1}{\rho_v}} \tag{4}$$

und diese Relation ist als eine Erweiterung des Krishnan'schen Reziprozitätsgesetzes (1) für schiefe Beobachtungsebenen zu betrachten; für horizontale Beobachtungsebene geht sie gleich (unter Übergang $P_v \rightarrow H_v$, $N_h \rightarrow V_h$ und unter der Bemerkung $H_v = V_h$) in die Gleichung (1) über. Durch diese Relation (4) ergibt sich, dass der Wert von ρ_u ausser von ρ_h und ρ_v nur noch von dem Quotienten P_v/N_h abhängig ist. Daraus ersieht man aber, dass die ganze experimentelle Prüfung des Reziprozitätsgesetzes für die schiefen Beobachtungebenen auf die Erforschung der Beziehung zwischen P_v und N_h gerichtet werden muss, weil nur unter einer solchen Erkenntnis die Gleichung (4) weiter transformiert werden kann. Dass dieser Quotient P_v/N_h von dem Neigungswinkel ψ der schiefen Beobachtungsebene zur Horizontalebene auf jeden Fall abhängen sein wird, scheint ausser Zweifel zu liegen; man braucht nur einen Blick auf die Formeln (6) und (7) dieser Abhandlung zu werfen.

* Die Definition von ρ_h ist in *Proc. Ind. Acad. Sci.*, 1935, **1**, 783 irrtümlichen weise reziprok abgedruckt (vgl. *Proc. Ind. Acad. Sci.*, (A), 1938, **7**, 22), wie dies aus der Definition in *Proc. Ind. Acad. Sci.*, (A), 1938, **7**, 22 und in *Koll.-ZS.*, 1938, **84**, 4 ersichtlich ist.

3. *Anwendung der Mie-schen Theorie*

Zum Schluss noch einige Bemerkungen hinsichtlich der Mie-schen Theorie. In meiner hier schon erwähnten früheren Abhandlung habe ich auf Grund der Mie-schen Theorie die Gleichung

$$\frac{N_v}{N_h} = \frac{P_h}{P_v} = \operatorname{ctg}^2 \psi \tag{5}$$

abgeleitet. Aus dieser Gleichung kann man zwei Gleichungen

$$\frac{P_v}{N_h} = \frac{P_h}{N_v} = \rho_v \operatorname{ctg}^2 \psi \tag{6}$$

und

$$\frac{N_v}{P_h} = \frac{N_h}{P_v} = \rho_h \operatorname{ctg}^2 \psi \tag{7}$$

ableiten, deren Anwendung an die Gleichung (4)

$$\rho_u = \rho_v \operatorname{ctg}^2 \psi \tag{8}$$

oder

$$\rho_u = \frac{1}{\rho_h} \operatorname{tg}^2 \psi \tag{9}$$

ergibt. Aus ihnen ergibt sich gleich weiter

$$\rho_h \rho_v \operatorname{ctg}^4 \psi = 1 \tag{10}$$

Die zwei Gleichungen (8) und (9) sind eine Art auf Grund der Mie-schen Theorie abgeleiteten Erweiterungen des Krishnan'schen Reziprozitätsgesetzes (1) für schräge Richtungen in den schiefen Beobachtungsebenen. Dem Sinne nach sie sind identisch mit der Relation (9) in meiner schon erwähnten Abhandlung.[4] Dass sie aber auch für die horizontale Beobachtungsebene (trotz den angeblichen unbestimmten Werten, zu denen sie durch einfaches Einsetzen von $\rho_h = \rho_v = 0$ für $\psi = 0$ führen), kann man leicht aus der Definition (2) ersehen, welche für $\psi = 0$ (wegen $P_v = H_v = 0$, $N_h = V_h = 0$, im Allgemeinen aber†) $P_h = H_h > 0$ und $N_v = V_v > 0$).

$$\rho_u = \frac{H_h}{V_v} \tag{11}$$

ergibt. Da die Gleichungen (8) und (9) für beliebig kleine (aber doch endliche) azimutale Winkel ψ ihre Gültigkeit noch immer behalten, so müssen wir auf Grund der Gleichung (11) und wegen der Stetigkeit der natürlichen Vorgänge verlangen, dass

$$\lim_{\psi \to 0} \rho_v \operatorname{ctg}^2 \psi = \frac{H_h}{V_v}$$

† Wie dies aus Fig. 3 auf S. 28 in *Proc. Ind. Acad. Sci.*, (A), 1938, **7** ersichtbar ist.

und auch

$$\lim_{\psi \to 0} \frac{\mathrm{tg}^2 \psi}{\rho_h} = \frac{H_h}{V_v}$$

wird.††

Aus demselben Grunde muss man auch verlangen, dass

$$\lim_{\psi \to 0} \rho_h \rho_v \, ctg^4 \psi = 1$$

wird.

Was die Frage nach der experimentellen Prüfung der Gleichungen (8) und (9), bzw. statt deren der Relation (10) betrifft, dürfe man eine Bestätigung derselben bei solchen verdünnten Kolloidal-Lösungen oder Emulsionen erwarten, wo die Voraussetzungen der Mie-schen Theorie annähernd erfüllt sind. Da nach der Mie-schen Theorie $H_v = V_h = 0$ sein muss, könnte man eine solche, bei einer kolloidalen Lösung oder Emulsion experimentell festgestellte Konstatation ($H_v = V_h = 0$) eventuell als einen Wegweiser dafür zu nehmen, dass eine weitere experimentelle Prufüng der Relation (10) zweckmässig ist.

4. Zusammenfassung

Der Zweck dieser Abhandlung ist, in erster Linie zu zeigen, in welcher Richtung eine experimentelle Forschung hinsichtlich der Erweiterung des Krishnan'schen Reziprozitätsgesetzes für schiefe Beobachtungsebenen aufzustellen ist. Durch die Diskussion der Formel (4) die ohne Rücksicht auf irgendwelche Zerstreuungstheorie und nur als sinnvolle Erweiterung des Krishnan'schen Reziprozitätsgesetzes aufgestellt wurde, ergab sich, dass es sich nur um die Erforschung des Verhältnisses $\frac{P_v}{N_h}$ handelt. Ausserdem wurde auf Grund der Mie-schen Theorie die Relation (10) für schiefe Beobachtungsebenen abgeleitet.

LITERATUR

1. R. S. Krishnan .. *Proc. Ind. Acad. Sci.*, (A), 1935, **1**, 782.
2. ———— .. *Kolloid-ZS.*, 1938, **84**, 2. In der Fussnote 12 auf der S. 4 ist die Gültigkeit des Reziprozitätsgesetzes für schräge Beugungsrichtungen in der Horizontalebene betont.
3. V. S. Vrkljan .. *Proc. Ind. Acad. Sci.*, (A) (Raman Band), 1938, **8**, 353.
4. Vgl. die Anmerkung (3).

†† In diesem Sinne $\left(\lim_{\psi \to 0} \frac{P_v}{N_h} = \frac{H_h}{V_v}\right)$ ist auch die Gültigkeit der Relation (9) in meiner früheren Abhandlung, *Proc. Ind. Acad. Sci.*, (A), 1938, **8**, 353, für horizontale Beobachtungsebene zu verstehen.

INTERFACIAL TENSION STUDIES ON MERCURY IN REACTING SYSTEMS*

By N. V. Rangaswamy Iyengar and Basrur Sanjiva Rao
(*From the Department of Chemistry, Central College, Bangalore*)

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Introduction

During the course of an investigation in this Laboratory on the reaction between hydrogen sulphide and sulphur dioxide in non-aqueous solutions, B. S. Rao and M. R. A. Rao[1] noticed that the gases did not interact in the presence of mercury or of carbon tetrachloride. When mercury, however, was brought in contact with a carbon tetrachloride solution of the two gases, reaction took place. The authors suggested that the primary product of the reaction between hydrogen sulphide and sulphur dioxide was thiosulphonic acid (thiosulphurous acid) and that its decomposition at the interface between mercury and carbon tetrachloride caused greater union between the two gases.

A systematic study of the interfacial tension of the system :

Solution of hydrogen sulphide and sulphur dioxide in carbon tetrachloride | Mercury

and of the allied system :

Solution of sulphur in carbon tetrachloride | Mercury

has now been carried out and the results are presented in this paper.

Experimental

Purification of Materials

Mercury.—Commercial mercury was passed several times in the form of fine spray through a column of dilute nitric acid containing 1% mercurous nitrate. The metal was then washed with water, dried at 200° C. and filtered through a pin-hole in filter-paper. The mercury was distilled in air under reduced pressure (25 mm.) and was again passed through a pin-hole in filter-paper to remove the oxide impurities. Finally, the air-distilled mercury was distilled twice in vacuum to free it from the last traces

* Thesis submitted by N. V. R. Iyengar in partial fulfilment of the requirements of the M.Sc. Degree Examination of the Mysore University.

of oxide ; and the purified product was stored in a phosphorus pentoxide desiccator.

Water.—Ordinary distilled water, after freeing it from carbon dioxide and ammonia was redistilled in an all-glass apparatus. The double-distilled water was suitably protected from contamination during storage.

Carbon tetrachloride.—Carbon tetrachloride of c.p. quality was kept over phosphorus pentoxide and mercury for some weeks with frequent shaking. The clear liquid was then decanted into a round-bottomed flask and distilled in an all-glass apparatus. Moisture was excluded by means of suitable guard tubes. The middle fraction boiling at 72·6° C. was collected and was preserved in glass-stoppered bottles. The liquid was freshly distilled before use.

Sulphur.—Merck's extra pure sulphur was used.

Sulphur dioxide.—Sulphur dioxide from a cylinder was dried over phosphorus pentoxide and was passed to saturation through pure dry carbon tetrachloride, atmospheric moisture being carefully excluded by means of suitable guard tubes.

Hydrogen sulphide.—Hydrogen sulphide was prepared by the action of water on aluminium sulphide. The sulphide had been prepared by the union between aluminium and sulphur on the lines of the thermite process. The gas, dried over phosphorus pentoxide, was passed through carbon tetrachloride to saturation. The resulting solution was carefully preserved.

The Technique of the Drop Weight Method

Harkins and co-workers[3,4,5] have standardized a method for the determination of surface tension of mercury by the drop-weight method. Their method consists in siphoning out mercury through a fine capillary tube bent twice at right angles, with one end of the tube dipping in a reservoir of mercury. The other end of the tube is well ground and serves as the dropping tip. Three to five drops are collected and weighed. The authors claim a high degree of accuracy.

In their apparatus for surface tension measurements, Bartell, Case and Brown[6] use a tip of razor edge sharpness obtained by cutting the capillary tube with a tungsten knife. They point out that drops formed at this tip are quite reproducible, being of uniform weight. They further state that drops formed at a tip obtained by grinding are bound to be non-uniform on account of the jaggedness of the tip. Our experiments confirm the above observations. A tip prepared by the method of Bartell and co-workers[6] has been employed in the present work. In order to get reproducible results it is necessary to regulate carefully the rate of formation of the drop.

For this purpose Harkins and co-workers employ a fine capillary. They observe that the capillary required is so fine that it often gets clogged. This difficulty has also been experienced by Gliddon[7] who has therefore devised a new arrangement for controlling the rate of formation of the drop. But his arrangement appears to be rather elaborate.

In the present work, the rate of formation of the drop is controlled by a simple device. The apparatus used (Fig. 1) consists of a flat-bottomed flask of about 125 c.c. capacity, a cooling column of fine capillary tube of U form to which the dropping tip is attached, through two ground glass joints G_1 and G_2 which move at right angles to one another, enabling one to secure the proper position of the tip. The edge of the tip is adjusted to be a level higher than any of the ground glass joints or stop-cocks so that no grease is needed for rendering the joints air-tight.

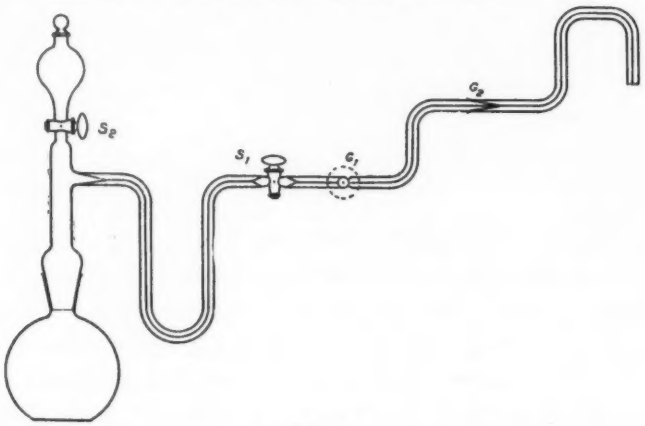

FIG. 1

The apparatus is set upon a reinforced concrete table, in order to avoid vibration. Air draughts are prevented by having proper screens. The apparatus is filled with purified mercury, all air bubbles being expelled. The capillary portion of the apparatus is filled by suitable manipulation of the stop-cocks and ground joints.

It is essential that the edge of the tip should be parallel to the surface. The drops obtained from a tube kept at an angle to the vertical do not form and tear off from a circular bore but from an elliptical one. Since the radius of the bore is involved in the calculations, it is obvious that an error will be introduced if the correct position for the tip is not secured. For this purpose a flat glass dish containing mercury is placed on an adjustable platform. The mercury surface is brought close to the tip. By observing

in between the edge and its reflection any tilt of the edge from the horizontal can be discovered and set right by operating the ground joints.

The drops are generated by gently warming the mercury reservoir by means of a carbon filament lamp. The rate of dropping can be controlled by adjusting the distance of the lamp from the reservoir. An asbestos sheet is used to screen the tip from the lamp.

The mercury drops are collected in clean weighing bottles (of known weight) kept ready in a desiccator. The first two drops are rejected in each case ; the subsequent drops are collected and weighed in batches of three to five drops.

To find out whether the drops formed are uniform in size, the weights of successive drops of mercury have been determined. The results of a typical experiment are indicated below.

TABLE I

No. of the drop	Weight of the drop in air	No. of drop	Weight of the drop in air
	gm.		gm.
1st	0·1527	9th	0·1521
2nd	0·1523	10th	0·1522
3rd	0·1520	15th	0·1520
4th	0·1522	20th	0·1522
5th	0·1518	26th	0·1518
6th	0·1520	30th	0·1519
7th	0·1521	32nd	0·1516
8th	0·1524	Mean	0·1520

As can be gathered from the above values the drops are quite uniform. The diameter of the inner bore of the tip is accurately measured by means of a " Photo-measuring Micrometer " which can be read correct to 0·001 mm. Measurements are made along eight even diameters and the average values employed in the calculations. The following formulæ have been used in the calculations.

(1) $T = \frac{Mg}{2\pi r} \cdot \frac{1}{F(a)}$ ....for surface tension of mercury ;

(2) $T = \frac{Mg}{2\pi r} \left\{\frac{\rho - \sigma}{\rho}\right\} \frac{1}{F(a)}$ ....for interfacial tension measurements,

where

M = mass of falling drop ;
r = radius of the bore ;
g = acceleration due to gravity ;
$F(a)$ = correction factor whose values are given by Harkins and co-workers ;
ρ = density of mercury at a known temperature ;
σ = density of the liquid at the same temperature.

Interfacial tension measurements are carried out in an exactly similar manner. A stoppered weighing bottle containing the freshly distilled liquid is kept near the tip for acclimatization. Meanwhile the first two drops are collected in a separate portion of the same liquid and rejected. After some time the stopper of the bottle is removed and the platform holding the weighing bottle is slowly raised until the tip is below the surface of the liquid. After collecting three to four drops of mercury the liquid is carefully removed by suction. The metal is then washed and dried at as low a temperature as practicable. In the case of water the mercury is washed with absolute alcohol a number of times and dried at 40° C. In general, six determinations have been made for each liquid. The results obtained are indicated in Table II.

TABLE II. *Tension Values of Mercury at Air, Water and Carbon Tetrachloride Interfaces at* 23·2° *C.*
(*Diameter of the Inner Bore* 0·1386 *cm.*)

Interface	Uncorrected drop weight	Correction factor (Harkins)	Tension dynes/cm.	Values obtained by	
				Harkins	Bartell
	gm.				
Air ..	0·1520	0·72024	473·9	464·4	..
Water ..	0·1272	0·71264	371·3	374·8	371·1
Carbon tetrachloride ..	0·1384	0·71510	373·7	362·2	..

Results

Having standardized the method of determinaion of surface tension by the method of drops, the interfacial tension of mercury in the following reacting systems has been measured.

(i) Mercury | Saturated solution of sulphur dioxide in carbon tetrachloride.

(ii) Mercury | Saturated solution of hydrogen sulphide in carbon tetrachloride.

(iii) Mercury | Carbon tetrachloride saturated with hydrogen sulphide and sulphur dioxide.

(iv) Mercury | Different dilutions of hydrogen sulphide and sulphur dioxide in carbon tetrachloride.

(v) Mercury | Sulphur in carbon tetrachloride at different concentrations.

The experimental error in these measurements is less than one dyne/cm.

It has to be noted that it is not practicable to carry out any interfacial tension measurements in system (v), when the sulphur concentration in carbon tetrachloride exceeds 0·05%, as the mercury drops get covered with sulphide rapidly and crumble to small droplets making the measurements impracticable. It may also be pointed out that the measurement of the interfacial tension of mercury cannot be made in carbon tetrachloride containing even minute quantities of dissolved iodine.

The results obtained are presented in Tables III and IV.

TABLE III. *Interfacial Tension between Mercury and Saturated Solutions of Hydrogen Sulphide and Sulphur Dioxide in Carbon Tetrachloride and their Mixtures at* 23·2° C.

Solution	Uncorrected drop weight	Correction factor (Harkins)	Interfacial tension dynes/cm.
	gm.		
Saturated solution of H_2S ..	0·1345	0·7153	372·6
Saturated solution of SO_2 ..	0·1292	0·71321	364·4
Mixtures of H_2S and SO_2 in CCl_4—			
(i) Saturated solution ..	0·1372	0·71593	379·9
(ii) Ten times diluted	0·1334	0·71470	370·1
(iii) Twenty times diluted ..	0·1340	0·71490	371·6
Pure carbon tetrachloride ..	0·1348	0·71510	373·7

TABLE IV. *Interfacial Tension between Mercury and Sulphur Solutions in Carbon Tetrachloride at 23·2° C.*

Concentration of sulphur in CCl_4 mg./100 g. of CCl_4	Uncorrected drop-weight gm.	Correction factor	Interfacial tension dynes/cm.
1. Pure CCl_4	0·1348	0·71510	373·3
2. 2·21 mg.	0·1470	0·71883	405·5
3. 6·66 mg.	0·1525	0·72007	419·9
4. 29·19 mg.	0·1555	0·72103	428·7
5. 32·12 mg.	0·1529	0·72047	420·7
6. 47·45 mg.	0·1500	0·72023	417·3

In an attempt to elucidate the nature of the changes in the interfacial tension in systems studied above, measurements have been made of the interfacial tension between mercury and aqueous solutions of complex salts of the metal.

The iodides and cyanides of mercury and potassium employed in the investigations are of A. R. quality.

Complex Iodide Solution.—Mercuric iodide prepared by interaction between aqueous solutions of mercuric chloride and potassium iodide is shaken up with molar potassium iodide to give a saturated solution. The complex iodide of mercury thus obtained is mixed with an equal volume of the stock potassium iodide and the resulting solution is used for the measurements, after suitable dilution.

The complex cyanide solution is prepared in the same manner as indicated above for the iodide. Densities of the solutions used have been measured at 23·5° C. using specific gravity bottles.

Interfacial tension between mercury and aqueous solutions at 23·5° C.

TABLE V. *Mercury and Aqueous Solutions of Potassium Iodide*

Concentration in moles of KI/litre	Uncorrected drop-weight gm.	Correction factor (Harkins)	Interfacial tension dynes/cm.
1. Pure water	0·1272	0·71264	371·3
2. 0·1 mol.	0·1012	0·70214	299·2
3. 0·5 ,, ...	0·1220	0·70675	361·4
4. 0·75 ,, ...	0·1115	0·70645	332·8
5. 1·00 ,, ...	0·1114	0·70787	339·6

TABLE VI. *Mercury and Aqueous Solutions of Potassium Mercuric Iodide*

Concentration in moles of HgI_2/litre	Uncorrected drop-weight gm.	Correction factor (Harkins)	Interfacial tension dynes/cm.
1. Pure water	0·1272	0·71264	371·3
2. 0·10 mol.	0·1122	0·70694	336·5
3. 0·50 ,, ...	0·0938	0·70013	282·9
4. 0·75 ,, ...	0·1163	0·70890	344·4
5. 1·00 ,, ...	0·1293	0·72220	374·1

TABLE VII. *Mercury and Aqueous Solutions of Potassium Cyanide*

Concentration in moles of KCN/litre	Uncorrected drop-weight gm.	Correction factor (Harkins)	Interfacial tension dynes/cm.
1. Pure water	0·1272	0·71264	371·3
2. 0·50 mol.	0·1100	0·70607	323·4
3. 1·00 ,, ...	0·1230	0·71710	361·6

TABLE VIII. *Mercury and Aqueous Solutions of Potassium Mercuric Cyanide*

Concentration in mols of $HgCy_2$/litre	Uncorrected drop-weight gm.	Correction factor (Harkins)	Interfacial tension dynes/cm.
1. Pure water	0·1272	0·71264	371·3
2. 0·50 mol.	0·1072	0·70501	315·2

Discussion

The results show that the lowering in interfacial tension of mercury in mixtures of carbon tetrachloride solutions of hydrogen sulphide and sulphur dioxide noticed by B. S. Rao and M. R. A. Rao[1] is confined to very dilute solutions and that with an increase in the concentration of the gases the interfacial tension actually rises. It is of interest to note that neither sulphur dioxide nor hydrogen sulphide can individually bring about any increase in the interfacial tension. With sulphur dioxide, in fact there is lowering in interfacial tension by several dynes.

With solutions of sulphur in carbon tetrachloride, the interfacial tension of mercury rises, reaches a maximum and then drops in value. There is in this case no initial fall in interfacial tension followed by a rise. Interfacial tension measurements in this system are practicable only when the solutions are so dilute that the rate of production of mecury sulphide is insignificant ; with iodine, which seems to react with mercury more vigorously, measurements are not practicable even in dilute solutions. The interfacial tension-concentration curve with solutions of sulphur in carbon tetrachloride is strongly suggestive of the usual electro-capillary curves obtained with mercury when aqueous solutions are used. Very little, however, is known at present about electro-capillary effects at mercury surfaces in contact with non-aqueous solutions ; for, the practical difficulties involved in studying such effects in non-conducting media seem to be very formidable.

We are of opinion that the initial decrease in interfacial tension noticed with mercury and aqueous solutions of complex salts, are due to adsorption phenomena while the subsequent increase in interfacial tension as the concentration of salt increases, is analogous to the effects noticed by Lenkewits[8] and Goebel[9] (*cf. International Critical Tables*, 1928, **4**, 439).

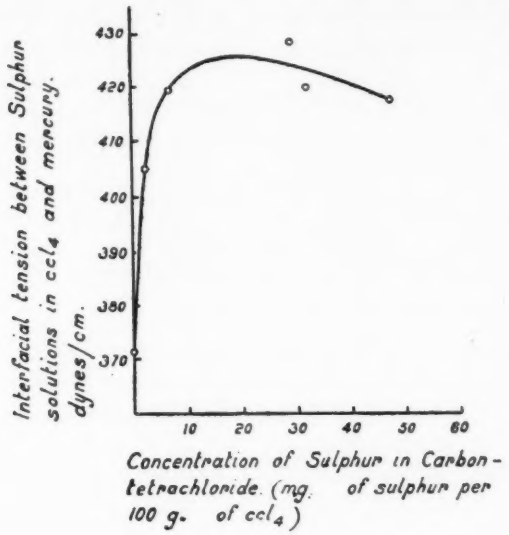

FIG. 2

The changes in interfacial tension with an increase in the concentration of the two gases (hydrogen sulphide and sulphur dioxide) cannot satisfactorily be explained on the basis of liberation of sulphur and the subsequent formation of the sulphide of mercury at the interface. The effect of concentration on the interfacial tension even in the simpler system (sulphur solution in carbon tetrachloride and mercury) does not at present admit of a satisfactory explanation and we are inclined to believe that interfacial tension changes of mercury in a chemically reactive system cannot profitably be studied by the technique adopted in this paper. We have tried using in the above systems the double capillary rise method described by Speakman[10] but the results are in no way encouraging.

Summary

A new method has been described for controlling the rate of formation of drops in the drop-weight method for the determination of surface tension and interfacial tension with mercury as one of the phases.

Interfacial tension of mercury has been measured in systems containing (*a*) hydrogen sulphide and sulphur dioxide in carbon tetrachloride solution, (*b*) sulphur in carbon tetrachloride solution, (*c*) potassium mercuric iodide in aqueous solution, and (*d*) potassium mercuric cyanide in aqueous solution. Certain interesting features of the results obtained, are discussed.

The authors desire to thank Mr. K. S. G. Doss, for his valuable assistance in the designing of the apparatus employed in these investigations.

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ON A SIMPLE SYSTEM OF CHARGED PARTICLES IN MILNE'S KINEMATICAL THEORY

By D. N. Moghe
(Research Scholar, Bombay University)

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1. Introduction

In a recent paper Milne[1] has defined mass, energy, force, work, etc., according to his kinematical theory. If the system of particles in his kinematical theory are supposed to be charged particles then some interesting results are obtained, it being assumed that the charge associated with the particles is the same for each particle. The value of the charge is e. The results obtained give an interpretation of the principal equations of the electro-magnetic field in terms of the kinematical theory of relativity.

Let us suppose that M is the momentum of any particle belonging to the kinematical system under consideration ; then

$$\mathrm{M} = (p, q, r), \tag{1}$$

where $p = mu$, etc., and $\mathrm{V} = (u, v, w)$. Therefore,

$$\frac{d}{dt}(mu) = e\mathrm{X} \tag{2}$$

is an equation of motion of any charged particle of the system. If, as a general case, these particles are supposed to collide with each other, then the loss of momentum due to the collision is proportional to the velocity of the particles and the equation (2) can be written in the general form, *viz.*,

$$\frac{d}{dt}(mu) = e\mathrm{X} - \mu u \tag{3}$$

In Part I of this paper we shall obtain the principal equations of electro-magnetism taking (2) as the equation of motion of any charged particle of the system ; and in Part II these very equations will be deduced, taking into account the collisions of these charged particles.

Milne defines force by the relation

$$\mathrm{F} \sim m\frac{d}{dt}\left(\mathrm{V} - \frac{\mathrm{P}}{t}\right), \tag{4}$$[2]

where F is the Newtonian measure of force, m is the Newtonian measure of the mass of an individual particle, and $\mathrm{V} - \frac{\mathrm{P}}{t}$ is the velocity of the constrained particle relative to its surroundings. $\frac{\mathrm{P}}{t}$ may be regarded as the cosmic velocity.

2. Part I : Non-colliding Particles

In the Maxwell-Lorentz theory of electro-magnetism, the electric force (X, Y, Z) and the magnetic force (α, β, γ) are determined by the equations, *viz.*,

$$\mathrm{X} = -\frac{\partial \phi}{\partial x} - \frac{\partial \mathrm{F}}{\partial t}, \text{ etc.} \tag{5}$$

and

$$\alpha = \frac{\partial \mathrm{H}}{\partial y} - \frac{\partial \mathrm{G}}{\partial z}, \text{ etc.,} \tag{6}$$

where $(-\mathrm{F}, -\mathrm{G}, -\mathrm{H}, \phi)$ is the electro-magnetic four vector denoting the electro-magnetic potential. It should be pointed out here that the electro-magnetic equations used in this paper are expressed in terms of Heaviside-Lorentz units.

If, during the motion, the mass m of each particle remains constant, then (2) can be written as

$$m\frac{du}{dt} = e\mathrm{X}. \tag{7}$$

As the particles are moving under the influence of the substratum, the x-component of the velocity of an individual particle will be $u - \frac{x}{t}$ instead of u. Therefore, we have from (4) and (7)

$$\mathrm{F}_x \sim m\frac{d}{dt}\left(u - \frac{x}{t}\right) = e\mathrm{X} \tag{8}$$

or, in vectorial form (8) can be expressed as

$$\mathrm{F} \sim m\frac{d}{dt}\left(\mathrm{V} - \frac{\mathrm{P}}{t}\right) = e\,(\mathrm{X}, \mathrm{Y}, \mathrm{Z}) \tag{9}$$

where $\mathrm{V} = (u, v, w)$ and $\mathrm{P} = (x, y, z)$. Taking the divergence of the electric force we have

$$e \operatorname{div} (\mathrm{X}, \mathrm{Y}, \mathrm{Z}) = m\frac{d}{dt}\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} - \frac{3}{t}\right) \tag{10}$$

Milne's equations for the motion of a system of particles in free space are given by the single vector relation, *viz.*,

$$\frac{d\mathrm{V}}{dt} = (\mathrm{P} - \mathrm{V}t)\frac{\mathrm{Y}}{\mathrm{X}}\,\mathrm{G}\,(\xi) \tag{11}^{3}$$

in the usual notation. For the fundamental system of particles $G(\xi) + 1 \to 0$, $X \to t^2$, $Y \to 1$, and $Z \to t$ so that (11) becomes

$$\frac{dV}{dt} \to -\frac{P - Vt}{t^2}. \tag{12}$$

If we regard the system of charged particles as the fundamental system then (10) reduces to

$$e \text{ div } (X, Y, Z) = \frac{m}{t} \text{ div } V = \text{div } \frac{mV}{t}. \tag{13}$$

Accordingly, we have

$$e\rho = \text{div } \frac{mV}{t}, \tag{14}$$

where ρ is the density of electric charge. From (13) follows

$$e\,(X, Y, Z) = \frac{mV}{t}. \tag{15}$$

If the influence of the substratum is negligible the average acceleration g of an individual particle is $\frac{V}{t}$. The relation (15) can now be expressed as

$$(X, Y, Z) = m'g, \tag{16}$$

where $m' = \frac{m}{e}$.

The Maxwellian equations of the electro-magnetic field are :

$$-\frac{d\alpha}{dt} = \frac{\partial Z}{\partial y} - \frac{\partial Y}{\partial z}, \text{ etc.,} \tag{17}$$

and

$$\frac{dX}{dt} + \sigma_x = \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z}, \text{ etc.,} \tag{18}$$

where $(\sigma_x, \sigma_y, \sigma_z)$ is the density of the electric current ; and as the current produced in the case under consideration is due only to charged particles in motion, we have

$$(\sigma_x, \sigma_y, \sigma_z) = \rho\,(u, v, w) = \rho V. \tag{19}$$

From the equations (17) and (15) we deduce

$$-\frac{dB}{dt} = \text{curl } \frac{mV}{et}, \tag{20}$$

where $B = (\alpha, \beta, \gamma)$. Also from equations (18), (15) and (19) we get the following relation to determine the magnetic vector B, *viz.*,

$$\text{curl } B = \rho V - \frac{mP}{et^3}. \tag{21}$$

The usual equation of continuity, *viz.*,

$$\frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial y}(\rho v) + \frac{\partial}{\partial z}(\rho w) + \frac{\partial \rho}{\partial t} = 0 \tag{22}$$

takes the form

$$m\rho\left(\text{div V} - \frac{3}{t}\right) + \text{F grad } \rho + m\frac{\partial \rho}{\partial t} = 0. \tag{23}$$

If ρ is not a function of position, grad $\rho = 0$; then ρ is given by the relation

$$\rho^{-1} = \frac{et^2}{2m} + \text{A}, \tag{24}$$

where A is a constant of integration. It follows from (24) that ρ decreases with time and that $\rho \to 0$ as $t \to \infty$. Also when $t \to 0$, $\rho \to \rho_0$, ρ_0 being the initial density of charge the constant of integration A is, therefore, equal to ρ_0^{-1}.

The mechanical stress (P, Q, R) in space due to the electro-magnetic field is given by

$$\text{P} = \rho\text{X} + \gamma\sigma_y - \beta\sigma_z, \text{ etc.} \tag{25}$$

Using (15) we obtain

$$(\text{P, Q, R}) = \rho\left(\frac{m\text{V}}{et} + [\text{B}\cdot\text{V}]\right). \tag{26}$$

The rate at which work is done by the mechanical force is

$$\frac{d\text{W}}{dt} = \text{X}\sigma_x + \text{Y}\sigma_y + \text{Z}\sigma_z = \frac{\rho m\text{V}^2}{et} = \left(\rho\text{V}\cdot\frac{m\text{V}}{et}\right) \tag{27}$$

and the Poynting flux $\pi = (\pi_x, \pi_y, \pi_z)$, where $\pi_x = \beta\text{Z} - \gamma\text{Y}$, etc., is expressed as

$$\pi = \frac{m}{et}[\text{B}\cdot\text{V}]. \tag{28}$$

It should be remembered that we are using the acceleration formula for the fundamental system as given by (12) for which

$$\text{F} \sim m\frac{d}{dt}\left(\text{V} - \frac{\text{P}}{t}\right) \to 0. \tag{29}$$

This simple value of the acceleration denoting a limiting state of the substratum is to be used only after the necessary operations have been performed. For instance,

$$e\,(\text{X, Y, Z}) = 0 \quad \text{for } \frac{d\text{V}}{dt} = -\frac{\text{P} - \text{V}t}{t^2}; \tag{30}$$

therefore,

$$e\rho = 0 \tag{31}$$

But the correct result is given by (14).

3. *Part II* : *Colliding Particles*

It is quite probable that the charged particles belonging to the kinematical system under consideration may have frequent collisions with each other. Let us assume, therefore, that the mass of each individual particle remains constant during the motion before and after the collisions. Hence, the equation corresponding to (7) can be written as

$$m\frac{du}{dt} = eX - \mu u, \tag{32}$$

so that the equations of motion for this case can be expressed by a single vector relation, *viz.*,

$$m\frac{dV}{dt}\left(V - \frac{P}{t}\right) = e\,(X, Y, Z) - \mu\left(V - \frac{P}{t}\right). \tag{33}$$

The divergence of the electric force would give the density of the electric charge as

$$e\rho = \text{div}\left[\frac{(m + \mu t)\,V}{t}\right] - \frac{3\mu}{t}; \tag{34}$$

but the equation of continuity (22) determines ρ more directly through a differential equation of the first order if we put grad $\rho = 0$ (*i.e.*, ρ is a function of t only), *viz.*,

$$\frac{d\rho^{-1}}{dt} + \frac{3m\rho^{-1}}{t\,(m + \mu t)} = \frac{et}{m + \mu t} \tag{35}$$

which integrates into

$$\rho^{-1} = \left(\frac{m}{t} + \mu\right)^3\left[A + \frac{4\,em}{\mu^5}\log\,(m + \mu t)\right] + me/3\mu^2 +$$

$$+ \frac{et}{\mu}[1 + 7m/\mu t + 10\,m^2/\mu^2t^2 + 4m^3/\mu^3t^3]. \tag{36}$$

A being a constant of integration. $\rho \to 0$ when $t \to \infty$.

From equations (17) and (18) we obtain the following formulæ to determine the magnetic force B, *viz.*,

$$-\frac{dB}{dt} = \text{curl}\left(\frac{mV}{et} + \frac{\mu V_1}{e}\right),\ V_1 = V - \frac{P}{t}, \tag{37}$$

and

$$\text{curl}\ B = \rho V - \frac{mP}{et^3}. \tag{38}$$

The mechanical stress brought into play by this system of charged particles in motion is given by

$$(P, Q, R) = \rho\left(\frac{mV}{et} + \frac{\mu V_1}{e} + [B \cdot V]\right) \tag{39}$$

and the work performed thereby is

$$\frac{dW}{dt} = \rho \left[\frac{mV^2}{et} + \frac{\mu e^2}{et} (Z - tY) \right] \text{ per unit time.} \qquad (40)^5$$

Lastly, the flow of energy per unit area or the Poynting flux π can be expressed as

$$\pi = \frac{m + \mu t}{et} \cdot [B \cdot V] - \frac{\mu}{et} [B \cdot P]. \qquad (41)$$

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[2] As a general case, let us take the force as given by

$$F = - MV (\xi - 1)/Z + Y^{-\frac{1}{2}} \frac{d}{dt} [Mg Y^{\frac{1}{2}} X/Z]$$

where $M = m\xi^{\frac{1}{2}}$, $g = - (P - VZ/Y)/X$, then the equation of motion for the system of charged particles (which cannot be called a simple system) is given after considerable reduction by

$$e (X, Y, Z) = - M (G + 1) [g + V (\xi - 1)/Z].$$

The fundamental system being given by $G + 1 \sim 0$, we have $e \sim 0$. This gives $F \sim 0$ for $G + 1 \sim 0$ which leads to relations of the form given by (4) and (12).

[3] Here $X = t^2 - \frac{P^2}{c^2}$, $Y = 1 - \frac{V^2}{c^2}$, and $Z = t - \frac{P \cdot V}{c^2}$ are not to be confused with the components of electric force denoted by the same letters.

[4] Here F is the electric force (X, Y, Z).

[5] Here as in reference (3) Y and Z are not to be confused with the components of electric force.

REACTION BETWEEN NITRIC ACID AND TIN IN PRESENCE OF CATALYSTS—PART II

By G. S. Kasbekar and A. R. Normand
(From the Department of Chemistry, Wilson College, Bombay)

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Introduction

In an earlier paper, the authors[2] (1937) while studying the reaction between nitric acid and tin in presence of catalysts suggested that the retarding effect of $NaHSO_3$ and Na_2SO_3 as due to the specific action of sodium ions. This view was supported by the observations made with other salts of sodium such as sodium chloride and sodium nitrate. A continuation of the same work, however, has thrown a considerable amount of light on this suggestion and forms the subject of this paper.

It was reported in the said paper that addition of 10 c.c. of a unimolar solution of NaCl to a reaction mixture of 50 c.c. of 0·14 gm./c.c. nitric acid and 0·7 gm. tin had prolonged the duration of reaction by 4·5 minutes (as compared to 7·0 minutes in its absence). A similar addition of unimolar solution of NaBr practically doubled this reaction period and it was further observed that the addition of same amount of a unimolar solution of NaI inhibited the reaction almost completely, for no trace of any action was noticed for weeks. A systematic study of the effect of the addition of solutions of varying concentrations of iodides of sodium, potassium and lithium was therefore carried out.

Experimental

The experimental procedure was similar to the one described in our previous paper.[2] At the end of each experiment the tin present in the solution in the stannous condition alone was estimated. Experimental observations are enumerated below.

In all these experiments 50 c.c. of nitric acid of 0·14 gm./c.c. concentration was used. The amount of tin employed was 0·7 gm. and 10 c.c. of the solution of the catalyst was added to the acid immediately before the addition of tin. The reactions were carried out at 30° C.

TABLE I. *Catalyst—Sodium Iodide*

Conc. of catalyst mols./litre	Time for tin to dissolve minutes	Tin in stannous form gm.
0·00	7·0	0·6258
0·033	30·0	0·6011
0·066	15·0	0·6370
0·132	15·0	0·6641
0·330	12·5	0·6083
0·50	About three-fourths of the tin was dissolved in 4 hours and solution was clear.	
0·66	About one-fourths of the tin was dissolved in 4 hours and the solution was clear.	
1·0	No reaction for three months, at the end of which period needle-shaped red crystals appeared in solution.	

TABLE II. *Catalyst : Potassium and Lithium Iodide**

Conc. of catalyst mols./litre	Time for tin to dissolve minutes	Tin in stannous form gm.
0·00	7·0	0·6258
0·033	8·5	0·5745
0·066	9·5	0·6161
0·132	13·0	0·6713
0·33	19 hrs.	0·5310
1·0	No reactions for three months, at the end of which needle-shaped red crystals appeared in solution.	

* Unimolar solution of lithium iodide gave results similar to a unimolar solution of potassium iodide above.

The behaviour of the alkali iodides when added to the reaction mixture was interesting. In small concentration they retarded the dissolution of tin. When 10 c.c. of their unimolar solution was added to the 50 c.c. of the reaction mixture they apparently completely inhibited the dissolution of tin for fully three months. During this period the reaction mixture with CO_2 above it was sealed air-tight in a glass bulb. It was, however, observed that six hours from the commencement of the reaction a yellow colouration developed four times in succession on the surface of the mixture, which disappeared on vigorous shaking. If instead of sealing the bulb, a continuous stream of CO_2 was allowed to bubble through the reaction mixture no such development of yellow colour was noticed. At the end of three months the tin in the sealed bulb was found to possess a red coating on its surface and to bear a shrivelled appearance. Needle-shaped red crystals were found first in the reaction mixture at the end of four and half months and in the following six weeks all the tin was replaced by these needles. If undisturbed these crystals were found to remain unchanged for over a year. On opening the sealed bulb, however, these fine crystals disappeared and a black precipitate was formed in the mixture, with the solution above it coloured red. The black precipitate was confirmed to be stannous oxide and the coloured solution contained free iodide. On analysis crystals were found to be those of stannous iodide.

With nitric acid of 0·2 gm./c.c. concentration there were no signs of any reaction or of the development of any colour for 48 hours, if a continuous stream of CO_2 was bubbling through the mixture. On sealing the mixture in a bulb the mixture showed no indications of any reaction for about an hour, but at the end of that time, a reddish colour was noticed which disappeared on vigorous shaking. The colour reappeared quickly and it was observed that the third time it made its appearance there were clear indications of a rapid action on tin and all the tin was turned into a black powder in less than a minute, leaving the solution above it coloured red. The black powder was again confirmed to be stannous oxide and free iodine was present in the liquid above.

Discussion

Earlier work had suggested a specific action of the alkali ion in retarding the velocity of the reaction. This suggestion would be further substantiated by the observations made with the use of alakli iodides. But the presence of alkali ions alone does not satisfactorily account for the complete inhibition of the reaction for almost three months, when molar solutions of the catalysts are employed. The formation of stannous iodide may be a result of a reaction between stannous nitrate and alkali iodide. This reaction has been

studied by P. Boullay[1] (1827), who was able to isolate the red needles of stannous iodide.

That the crystals appeared after the tin had turned red, seems to indicate that the formation of stannous iodide is not due to the double decomposition but is caused by the action of HI on tin. That hydroidic acid acts on tin and forms stannous iodide was shown by J. Personne[3] (1862). The development of the colouration in the mixture is obviously caused by the oxidation of HI by nitric acid to free iodine. The discharging of the colour on shaking is attributed to the surface action of tin in the mixture, for it was found that addition of metallic tin to a mixture of KI and HNO_3, which had developed a yellow colour, discharged the colour immediately.

It seems, therefore, reasonable to ascribe the retardation mainly to the formation of a layer of stannous iodide, on the surface of tin, which being insoluble in nitric acid, protects the metal from further action. The appearance of tin at the end of four months points to the same conclusion. It also appears that the reaction velocity is governed to a large extent by the concentration of HI and its oxidation products. The fact that during the experiment with 0·2 gm./c.c. nitric acid, the reaction did not take place when the CO_2 was being bubbled through, adds an argument in favour of the above suggestion. For in this case the products of oxidation of HI would be removed from the reaction mixture, by the bubbling carbon dioxide. This also explains the non-formation of the red colouration during the same experiment.

As higher concentrations of nitric acid would cause a more rapid oxidation of HI and a more frequent development of colour, a more vigorous reaction with the metal would be naturally expected. This expectation is borne out by experimental observations. The non-formation of stannous iodide in such cases is due to its instantaneous decomposition by the nitric acid.

Summary

1. Iodides of sodium and potassium retard the reaction between nitric acid and tin. This retardation may be due to the specific action of the alkali ions as suggested in the earlier paper.

2. Unimolar solutions of NaI, KI and LiI inhibit the reaction for about three months and thereafter cause the formation of a thin layer of stannous iodide on the surface of tin and the formation of the oxidation products of HI in the reaction mixture are responsible for this behaviour.

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ON THE STABILITY OF MOTION IN MILNE'S KINEMATICAL SYSTEM

By D. N. Moghe

(*Research Scholar, Bombay University*)

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The set of particles receding from the central mass-condensation forms as a whole the Kinematical System in statistical motion given by the formula for the acceleration of an individual particle of the system, *viz.*,

$$\ddot{r} = -(r - \dot{r}t)\frac{Y}{X} - (r - \dot{r}t)\frac{Y}{X}\cdot\frac{C}{(\xi - 1)^{\frac{3}{2}}\psi(\xi)}\cdot^{1} \qquad (1)$$

This formula gives the trajectories of the system of particles under consideration so that equations of small motion can be determined from it. Let us take, for instance, a radius vector $r = r_0$ in the neighbourhood of which the equations of small motion are to be studied. For this a necessary assumption is that the following conditions hold good, *viz.*,

$$(\dot{r})_{r=r_0} = 0, \qquad (\ddot{r})_{r=r_0} = 0. \qquad (2)$$

Let us, then, put $r = r_0 + \epsilon$. Here it is assumed that the particle at r_0 is displaced to the neighbouring position $r_0 + \epsilon$. The values of the functions X, Y, Z and ξ for the displaced position of the particle are given by the following formulæ :

$$X = X_0 - \frac{2r_0\epsilon}{c^2},\ Y = Y_0 - \frac{2\dot{r}_0\dot{\epsilon}}{c^2},\ Z = Z_0 - \frac{r_0\dot{\epsilon} + \dot{r}_0\epsilon}{c^2} \qquad (3)$$

and
$$\xi = \xi_0\left[1 + \frac{2}{c^2}\left\{\frac{r_0\epsilon}{X_0} + \frac{\dot{r}_0\dot{\epsilon}}{Y_0} - \frac{r_0\dot{\epsilon} + \dot{r}_0\epsilon}{Z_0}\right\}\right]. \qquad (4)$$

Also
$$\frac{Y}{X} = \frac{Y_0}{X_0}\left[1 + \frac{2}{c^2}\left\{\frac{r_0\epsilon}{X_0} - \frac{\dot{r}_0\dot{\epsilon}}{Y_0}\right\}\right], \quad \text{where } X_0 = t^2 - \frac{r_0^2}{c^2}, \text{ etc.} \qquad (5)$$

All these values are calculated correct to the first order of small quantities.

The equations corresponding to (1) for the displaced and the undisplaced positions can now be written as

$$\ddot{r}_0 + \ddot{\epsilon} = -(r_0 - \dot{r}_0 t + \epsilon - \dot{\epsilon}t)\frac{Y_0}{X_0}\left[1 + \frac{2}{c^2}\left\{\frac{r_0\epsilon}{X_0} - \frac{\dot{r}_0\dot{\epsilon}}{Y_0}\right\}\right]$$

$$-(r_0 - \dot{r}_0 t + \epsilon - \dot{\epsilon}t)\frac{Y_0}{X_0}\left[1 + \frac{2}{c^2}\left\{\frac{r_0\epsilon}{X_0} - \frac{\dot{r}_0\dot{\epsilon}}{Y_0}\right\} - \left\{\frac{3\xi_0}{c^2(\xi_0 - 1)} + \frac{2\xi_0\psi'(\xi_0)}{c^2\psi(\xi_0)}\right\} \times\right.$$

$$\left. \times \left\{\frac{r_0\epsilon}{X_0} + \frac{\dot{r}_0\dot{\epsilon}}{Y_0} - \frac{r_0\dot{\epsilon} + \dot{r}_0\epsilon}{Z_0}\right\}\right] \frac{C}{(\xi_0 - 1)^{\frac{3}{2}}\psi(\xi_0)} \tag{6}$$

and $$\ddot{r}_0 = -(r_0 - \dot{r}_0 t)\frac{Y_0}{X_0} - (r_0 - \dot{r}_0 t)\frac{Y_0}{X_0}\frac{C}{(\xi_0 - 1)^{\frac{3}{2}}\psi(\xi_0)}. \tag{7}$$

Therefore, from equations (6) and (7) we get the following equation for small motion about the position $r = r_0$:

$$\ddot{\epsilon} = -\left[(\epsilon - \dot{\epsilon}t) + \frac{2(r_0 - \dot{r}_0 t)}{c^2}\left\{\frac{r_0\epsilon}{X_0} - \frac{\dot{r}_0\dot{\epsilon}}{Y_0}\right\}\right]\frac{Y_0}{X_0} -$$

$$-\left[(\epsilon - \dot{\epsilon}t) + \frac{2(r_0 - \dot{r}_0 t)}{c^2}\left\{\frac{r_0\epsilon}{X_0} - \frac{\dot{r}_0\dot{\epsilon}}{Y_0}\right\} -\right.$$

$$\left. - \frac{(r_0 - \dot{r}_0 t)}{c^2}\left\{\frac{3\xi_0}{(\xi_0 - 1)} + \frac{2\xi_0\psi'(\xi_9)}{\psi(\xi_0)}\right\}\left\{\frac{r_0\epsilon}{X_0} + \frac{\dot{r}_0\dot{\epsilon}}{Y_0} - \frac{r_0\dot{\epsilon} + \dot{r}_0\epsilon}{Z_0}\right\}\right]$$

$$\times \frac{C}{(\zeta_0 - 1)^{\frac{3}{2}}\psi(\xi_0)}. \tag{8}$$

If the origin of co-ordinates be taken at $(r_0, \dot{r}_0, t)$, then we have

$$\ddot{\epsilon} = -(\epsilon - \dot{\epsilon}t)\frac{Y_0}{X_0} - (\epsilon - \dot{\epsilon}t)\frac{Y_0}{X_0}\frac{C}{(\xi_0 - 1)^{\frac{3}{2}}\psi(\xi_0)}. \tag{9}$$

The form of equation (9) being the same as that of (1) we can draw a conclusion from this that the state of equilibrium whether stable or unstable of a particle belonging to the system under consideration persists at all times. In equation (9) let us consider only the first term on the r.h.s. After two quadratures we get the value of the displacement as

$$\epsilon = at + bt\log t. \tag{10}$$

This goes to point out that the motion is unstable.

It will be worth while to study the same problem from the point of view of the General Theory of Relativity. Walker[2] has given the following

line element for Milne's case, *viz.*,

$$ds^2 = \{F(X)\}^2 \left[dt^2 - \frac{1}{c^2}(dx^2 + dy^2 + dz^2) \right]. \tag{11}$$

The well-known condition that the motion of the particle be stable is that the following relations hold good :

$$\{44, \alpha\} = 0, \quad (\alpha = 1, 2, 3). \tag{12}$$

In the present case we have $\{44, \alpha\} = -\frac{2x^\alpha}{F}\frac{dF}{dX}$, $x^\alpha \equiv (x, y, z)$ which does not satisfy the conditions (12). The conditions (12) are only satisfied for the system of particles described by $G(\xi) = -1$ which gives the " line-element of the substratum ".[3]

The geodesic equations of motion for the system of particles are given by the relation

$$\left.\begin{aligned} \frac{d^2x^\alpha}{dt^2} + \{\mu\nu, \alpha\}\frac{dx^\mu}{dt}\frac{dx^\nu}{dt} - \{\mu\nu, 4\}\frac{dx^\alpha}{dt}\frac{dx^\mu}{dt}\frac{dx^\nu}{dt} = 0, \\ (\mu, \nu = 1, 2, 3, 4\,; \quad \alpha = 1, 2, 3). \end{aligned}\right\} \tag{13}$$

If (x_0, y_0, z_0) describes the equilibrium position for any individual particle belonging to the system at the particular epoch t, and (ξ, η, ζ) gives a small displacement about the equilibrium position, then the equations of small motion can be written down as

$$\ddot{\xi} + (2\{14, 1\} - \{44, 4\})\dot{\xi} = 0, \tag{14}$$

$$\ddot{\eta} + (2\{24, 2\} - \{44, 4\})\dot{\eta} = 0, \tag{15}$$

and

$$\ddot{\zeta} + (2\{34, 3\} - \{44, 4\})\dot{\zeta} = 0, \tag{16}$$

where the three-index symbols are to be calculated for the line-element (11). Accordingly equation (14) can be rewritten as follows :

$$\ddot{\xi} - \left(\frac{4x}{c^2} + 2t\right)\frac{d\log F(X)}{dX}\cdot\dot{\xi} = 0. \tag{17}$$

Similarly, for (15) and (16) we get

$$\ddot{\eta} - \left(\frac{4y}{c^2} + 2t\right)\frac{d\log F(X)}{dX}\cdot\dot{\eta} = 0, \tag{18}$$

and

$$\ddot{\zeta} - \left(\frac{4z}{c^2} + 2t\right)\frac{d\log F(X)}{dX}\cdot\dot{\zeta} = 0. \tag{19}$$

From these last three equations it can be shown that the necessary and sufficient conditions for the stability of motion of the system of particles

is that

$$\frac{d \log F(X)}{dX} < 0.^4 \qquad (20)$$

Thus it is found that although Milne has taken a static space to describe the motion of a system of particles according to his Kinematical Theory of Relativity, this motion is not in general stable ; it is found to be stable only in the particular case given by $G(\zeta) = -1$ which determines the so-called substratum in its essence. There is, however, a peculiarity about the motion of the particles belonging to this system as determined by equation (1) : That the state of equilibrium whether stable or unstable is independent of the position of the particular particle whose motion is being studied as a model and it is also independent of the epoch.

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MAGNETIC PROPERTIES OF COPPER AMALGAMS

By S. S. Bhatnagar,
P. L. Kapur and Girdharilal Mittal
(*From the University Chemical Laboratories, Lahore*)

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The magnetic behaviour of copper in dilute copper amalgams has recently elicited some controversy. One of us[1] observed that dilute copper amalgams of low copper content are merely mechanical mixtures of the two metals and the magnetic susceptibility values vary from that of pure copper to that of pure mercury. Bates and Tai[2] observed that of all the metals which are diamagnetic in the solid state, only copper retained its diamagnetic character in amalgams of dilute concentrations, whereas elements like bismuth became paramagnetic.

Venkataramaiah[3] has, however, recently reported that even copper became paramagnetic in dilute amalgams and as this claim requires further examination, the difference in the magnetic behaviour of copper in dilute amalgams observed by different workers may be due to the variations in the conditions under which the experiments might have been conducted. Amalgams were, therefore, prepared under definite conditions and the magnetic susceptibility of the samples prepared were determined on a Gouy's balance and were further checked on the Bhatnagar-Mathur Magnetic Interference Balance.[4]

Experimental

For the preparation of amalgams, pure mercury prepared by the Bijlmann[5] method and finally distilled in a small pyrex retort was used throughout.

As the magnetic susceptibility value of mercury itself has been established correctly only recently, the value obtained by us has been compared by those obtained by other workers.

The magnetic susceptibility value of mercury observed by Honda and Owen, was different in different magnetic fields, so they applied a correction and obtained the magnetic susceptibility value of mercury as $-0 \cdot 184 \times 10^{-6}$. This value was taken to be correct until Vogt found that single crystal of mercury in liquid and in solid state has the magnetic susceptibility value

$-0\cdot168 \times 10^{-6}$. Since then the magnetic susceptibility value $-0\cdot168 \times 10^{-6}$ for mercury has been confirmed by Bates and Tai and by Bhatnagar and Nevgi. From Table I it is clear that the value obtained by the

TABLE I

Authority	Magnetic Susceptibility $\times 10^6$
Authors	$-0\cdot165$
Honda and Owen[6]	$-0\cdot190$
Owen[7]	$-0\cdot184$
Davis and Keeping[8]	$-0\cdot189$
Vogt[9]	$-0\cdot168$
Bates and Tai[2]	$-0\cdot169$
Bhatnagar and Nevgi[10] ..	$-0\cdot157$

authors is in very good agreement with that obtained recently by other workers.

In order to prepare an amalgam by electrolysis, weighed amount of annalar copper sulphate was dissolved in 20 c.c. of water in a pyrex test-tube of one inch diameter and a weighed amount of mercury was taken and made the cathode. The anode was a platinum wire which just dipped under the surface of the solution. In order to find the weight of copper that went in solution in mercury, another tube containing the same concentration of copper sulphate and having a platinum foil as a cathode and platinum wire as an anode was palced in series. The increase in weight of platinum foil after electrolysis gave the amount of copper that went in solution in mercury.

The current used was from lead storage batteries and was of the order of 10–20 milliamperes depending on the concentration of solution. The magnetic susceptibility values of the amalgams prepared by the above method are given in Table II.

TABLE II

Percentage of copper in amalgams	Magnetic Susceptibility × 10^6	
	Observed	Calculated
0·5	— 0·162	— 0·165
1·0	— 0·161	— 0·164
2·0	— 0·159	— 0·163
3·0	— 0·159	— 0·162

The values given in column 3 are calculated on the mixture law, assuming the mass susceptibility value of copper to be $-0{\cdot}086 \times 10^{-6}$, as given in *International Critical Tables*. It is clear from the results that the observed value for magnetic susceptibility of amalgams is lower than the calculated one, indicating that the amalgams have become paramagnetic. It is argued, however, that the observed lowering of the susceptibility of amalgams may be due to the fact that magnetic susceptibility of copper actually formed during the process of electrolysis, may be different from that given in the *International Critical Tables* owing to the chances of oxidation under conditions of electrolysis.

To verify it the susceptibility value of copper, obtained by the electrolysis of annalar copper sulphate, was determined and is given below in Table III, along with the values obtained by other workers.

TABLE III

Authority	Magnetic Susceptibility Value × 10^6
Honda and Shiminza ..	— 0·084
Rao	— 0·080
Inter. Crit. Tables ..	— 0·083
Authors	— 0·048

It is well known that copper at room temperature has the tendency to form oxides, which are paramagnetic. The low magnetic susceptibility value of copper may be due to the formation of such oxides, when copper sulphate solution is being electrolysed at ordinary temperature. So to avoid oxidation annalar copper sulphate was electrolysed in ice-cold solution. The susceptibility value of the samples of copper thus prepared was found to be $-0{\cdot}073 \times 10^{-6}$, a value higher than the previous ones, but still lower than the values observed by other workers.

Annalar copper sulphate contained 0·014 per cent. of iron, therefore, the lower value of copper observed may be due to its contamination with iron. Pure copper sulphate was, therefore, obtained by dissolving pure copper, prepared by the following method, in concentrated sulphuric acid.

Preparation of pure copper.—Rao's method of preparing copper co-agula by sparkling between the copper electrodes in a medium of inert liquid (propyl alcohol) was abandoned, because it was found that considerable amount of carbon was obtained along with copper in spite of all precautions.

Copper was, therefore, prepared by shaking a ten per cent. solution of annalar copper sulphate with extra pure granulated zinc metal. When copper had been completely displaced from the solution, *i.e.*, when the solution became colourless, the precipitate was washed with distilled water and refluxed with conc. hydrochloric acid and later on boiled, washed with dilute, pure hydrochloric acid (1·1) two or three times. It was kept under very dilute hydrochloric acid, so that if any oxide was formed, it was at once redissolved in it and in this manner, copper could be kept without oxidation for about a fortnight. The copper was washed free of hydrochloric acid and then washed with alcohol and subsequently with ether and was ultimately dried under vacuum at about 60° C. Its magnetic susceptibility value was found to be $-0{\cdot}085 \times 10^{-6}$ which is in very good agreement with the value obtained by other workers.

This copper was dissolved in pure sulphuric acid and diluted with water to get pure copper sulphate solution, which was used as an electrolyte to prepare amalgams by electrolysis at low temperatures.

The percentage of copper present in the amalgams prepared from the pure copper sulphate was determined iodometrically and also by electrodeposition method. The results obtained by both the methods were in excellent agreement.

The magnetic susceptibility values of these amalgams are given in Table IV.

TABLE IV

Percentage of copper in amalgams	Magnetic Susceptibility $\times 10^6$	
	Observed	Calculated
0·49	− 0·164	− 0·165
0·99	− 0·164	− 0·164
1·25	− 0·163	− 0·163
2·00	− 0·162	− 0·163
3·00	− 0·161	− 161
4·00	− 0·160	− 160
5·00	− 0·159	− 160
7·5 (Hard)	− 0·139	− 0·159
10·00 (Hard)	− 0·125	− 0·157

Amalgams upto 5 per cent. concentration of copper took a few hours to be prepared and remained fluids, but those containing higher percentage of copper took two to three days to be prepared and these hardened during the course of electrolysis.

It is clear from the above table that as long as the amalgams could be obtained in the fluid state, *i.e.*, upto 5 per cent. of copper concentration their observed and the calculated susceptibility values agree very well, but the amalgams of higher concentrations which solidify give lower susceptibility values than the calculated ones. This lowering in the values may be due to the oxidation of copper to some paramagnetic compounds during the course of electrolysis for a long time or due to a change in crystal structure which imparts the hardened structure.

Therefore amalgams containing higher percentage of copper were alternatively prepared by grinding the components in right proportions under very dilute analytically pure sulphuric acid.

The magnetic susceptibility value of fresh and dry amalgams prepared by the above method are tabulated below and in column 3 are given the calculated values according to the mixture law.

TABLE V

Percentage of copper in gm. in amalgams	Magnetic Susceptibility × 10^6	
	Observed	Calculated
10	− 0·156	− 0·157
20	− 0·147	− 0·148
30	− 0·140	− 0·140
34	− 0·138	− 0·138
40	− 0·131	− 0·132
50	− 0·125	− 0·125
60	− 0·116	− 0·117
70	− 0·109	− 0·110
80	− 0·099	− 0·100
90	− 0·091	− 0·091

From the results, it is clear that the observed magnetic susceptibility values of the freshly prepared amalgams are in very good accord with the calculated ones. It was, however, observed that amalgams hardened on keeping and their magnetic susceptibility value diminished very much.

The magnetic susceptibility values of some of these are given below in Table VI.

TABLE VI

Percentage of copper amalgams	Magnetic Susceptibility × 10^6	
	After keeping for a week	Calculated
40	− 0·071	− 0·141
50	− 0·059	− 0·131
60	− 0·051	− 0·117

It may be contended that the lowering in magnetic susceptibility value of amalgams on keeping in air may be due to the oxidation of copper. Therefore, in order to avoid the oxidation of copper freshly prepared amalgams were either kept under ether or in a vacuum desiccator. In spite of this it was observed that the magnetic susceptibility value of these amalgams went on decreasing. These samples were analysed to find if any oxide was formed and it revealed that the hardened black and brittle sample of amalgam containing 34 per cent. copper, after keeping under ether, contained 33·03 per cent. of copper and the other after keeping in vacuum contained 33·98 per cent. of copper. The fall in the percentage of copper in the samples kept in air is probably due to the formation of some oxides. Therefore, the greater fall in susceptibility value of the samples kept in air seems to be due to the formation of copper oxide which is known to be paramagnetic. Fresh amalgams prepared by grinding method were therefore at once sealed under vacuum in pyrex tubes which had been previously heated upto about 500° C. to expel all occluded oxygen and other gases from the glass lest the occluded gases should affect the amalgams in any way. The viscosity and colour of such amalgams remained nearly the same for about two days but after that they became more viscous and finally solid and then their colour faded. Their magnetic susceptibilities were determined in terms of pull per gram on the Gouy's balance from day to day, till the deflection became constant. The susceptibility values determined from these observations are tabulated in Table VII along with the susceptibility value of freshly prepared amalgams. In column 4 are given the difference between the susceptibilities of fresh and aged amalgams.

TABLE VII

Percentage of copper in amalgam	Magnetic Susceptibility × 10^6		Difference 10
	Fresh amalgam	Old amalgam	
5·0	− 0·159	− 0·093	0·066
10·0	− 0·156	− 0·087	0·069
20·0	− 0·147	− 0·070	0·077
30·0	− 0·140	− 0·055	0·085
34·0	− 0·136	− 0·047	0·089
40·0	− 0·132	− 0·051	0·081
50·0	− 0·124	− 0·048	0·076
60·0	− 0·116	− 0·046	0·070
70·0	− 0·107	− 0·041	0·066
80·0	− 0·099	− 0·035	0·064
90·0	− 0·091	− 0 029	0·062

Discussion of Results

From the results tabulated in Table IV it is clear that freshly prepared amalgams obey the mixture law and on hardening the magnetic susceptibility value falls ; the difference between the magnetic susceptibility values of the freshly prepared and hardened amalgams varies with the varying concentrations, being maximum in the case of amalgam containing 34 per cent. copper.

One of us (S. S. Bhatnagar) while working on very dilute copper amalgams prepared by electrolysis, found that the magnetic susceptibility values of amalgams vary linearly from that of mercury to that of copper. Bates and Tai[2] determined the magnetic susceptibility of series of amalgams of dilute concentrations of manganese, bismuth, chromium and copper and found that with the exception of copper, all the metals which are diamagnetic in solid state, became paragmanetic in dilute amalgams. The

paramagnetism of the metal in amalgams is attributed by them to the increase of free electrons in dilute amalgams. This view is further supported by the work of Skaupy,[11] who refers to the well-known fact that conductivities of such amalgams containing the metals like lead, zinc, cadmium, etc., are greater than those of pure mercury, whereas the conductivities of solid solutions or of mixed crystals are always less than that of solvent metal. He attributes this conductivity behaviour of amalgams to the increase in number of the free electrons. Venkataramaiah[3] has also studied recently the magnetic properties of dilute amalgams of copper and has found that the observed magnetic susceptibility value of dilute copper amalgam is lower than the calculated ones. He has attributed this change to the increase in the number of free electrons in dilute amalgams of copper as in those of other metals.

These results of his are contrary to those observed by Bates and Tai and by the authors. He prepared the amalgams by the electrolysis of pure copper sulphate and assumed the magnetic susceptibility of copper to be $-0{\cdot}083 \times 10^{-6}$ from the International Critical Tables. It has been shown by us that this procedure is not justified as in the process of prolonged electrolysis in presence of air and due to heat generated, copper gets oxidised and there is no justification in amalgams so prepared to employ the value for copper given in the International Critical Tables.

Fresh support in favour of our work comes from the work of Terry and Wright[12] who have investigated the crystal structure of concentrated copper amalgams by X-ray study and have found that freshly prepared amalgams of copper are mechanical mixtures but that they change the crystal structure on hardening. They have also found that there is a special change in the crystal structure in amalgams ranging from 30–35 per cent. of copper, indicating the formation of a compound at these concentrations.

From the magnetic data given in Tables IV and V, it is evident that freshly prepared amalgams are just mechanical mixtures and that on hardening, they form compounds and that in case of 34 per cent. of copper amalgam, the change is more marked and hence shows the formation of a compound at that concentration.

Summary

Magnetic properties of dilute as well as concentrated amalgams have been investigated. It has been shown that when dilute amalgams are prepared by prolonged electrolysis at room temperature the diamagnetic susceptibilty of the amalgams prepared is lower than that calculated on the

mixture law and the results are in line with those of Venkataramiah ; but if the amalgams are prepared at low temperature, 0° C., within 4–5 hours or by grinding the components according to the method of Terry and Wright susceptibility value of the amalgams obeys the mixture law. This difference in the susceptibility has been explained by the authors, by suggesting the formation of paragmanetic oxides formed during prolonged electrolysis at high temperatures. Amalgams of higher concentrations prepared by grinding method, when fresh obey the mixture law but on keeping, even under vacuum, become less diamagnetic and the maximum difference, in susceptibility values between a fresh and an aged amalgam is observed in one which contains 34 per cent. copper. This is supposed to be due to the formation of compound.

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COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE ORGANIC AND INORGANIC SALTS OF ISONITROSO-PYRAZOLONES AND ISOOXAZOLONES

By Sikhibhushan Dutt
and
(Miss) Ione Nitravati Dharam Dass
(From the Chemistry Department, Allahabad University)

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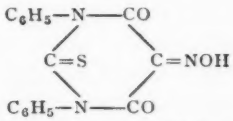
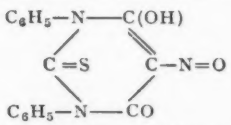
In a previous communication by the present authors,[1] it has been shown that isonitrosodiphenyl-thiobarbituric acid or diphenylthio-violuric acid, which is an orange coloured crystalline compound with the following constitution (I) :



(I) Diphenylthio-violuric acid (Oximino-ketonic form)

forms intensely coloured blue or green salts with alkalies or organic bases, the transition of colour from orange to blue or green being sufficiently strong and sharp for the substance to act as an excellent indicator. The change of colour by the action of alkalies or organic bases has been shown from theoretical considerations to be due to structural change from the above oximino-ketonic (I) to a nitroso-enolic structure (II) given below :



(II) Diphenylthio-violuric acid (Nitroso-enolic form)

This form is more acidic than the oximino-ketonic form, and consequently can produce better salts by complete neutralisation with alkalies and organic bases. And once the nitroso-enolic form becomes stabilised by salt formation, it cannot revert back into the oximino-ketonic form by a process of tautomerisation involving the transference of a hydrogen atom. The nitroso-enolic form in which the constitution of the molecule becomes fixed by salt formation, contains a highly strained nitroso-(N = O) group

which, according to a " Theory of colour on the basis of molecular strain " advanced by Dutt,[2] is the most highly absorptive of all organic groupings, and is consequently the most fruitful cause of intense colour amongst comparatively simple organic compounds. And this has been shown to be the cause of intense colour of organic and inorganic salts of violuric acid by Ghatak and Dutt,[3] of violantin and alloxantin by Gaind and Dutt,[4] of thiovioluric acid by Lal and Dutt[5] and of diphenyl-violuric acid by Prakash and Dutt,[6] the slight differences in the absorption spectra of these various classes of substances being due to differences in the character and molecular weight of groups or radicals attached to the main nucleus of malonyl-urea contained in all of them.

In the present investigation, the problem has been attacked from a different point of view, particularly in relation to substances which do not contain the above-mentioned nucleus in their molecular structure. The compounds that have been taken for the investigation are isonitroso-3-methyl-isooxazolone (III) and isonitroso-3-phenyl-isooxazolone (IV) which have been found to react with alkalies and organic bases with formation of crimson and violet salts respectively, although the free acids are practically colourless, and dissolve in organic solvents to colourless solutions. In these cases also there is not the slightest doubt that the tremendous change of colour brought about by salt formation with alkalies and organic bases must be due to fundamental changes in the constitution of the molecules from oxinimo-ketonic (III and IV) to nitroso-enolic (V and VI) forms as shown in the following diagrams :

Isonitroso-isooxazolones

Oximino-ketonic forms — Nitroso-enolic forms

(III) R = Me : Isonitroso-3-methylisooxazolone (V) Do.

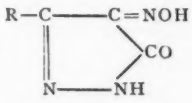
(IV) R = Ph : Isonitroso-3-phenylisooxazolone (VI) Do.

Both isonitroso-3-methyl-, and isonitroso-3-phenyl-isooxazolones dissolve in water and the concentrated aqueous solutions are almost colourless, or at best have only a pale cream coloration like the solids themselves. But on large dilution, a pale pink colour is developed in both the cases which is very characteristic of these substances, and they are in this respect quite analogous to violuric acid which also exhibits such a phenomenon. From this it is also quite apparent that isonitroso-3-methyl, and isonitroso-3-phenyl-isooxazolones must have configurations which are tautomeric

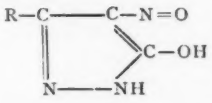
between (III) and (V) and also (IV) and (VI) respectively, according to existing circumstances, and the same argument with regard to their colour phenomena can be adduced as have been given in the cases of diphenylthiovioluric acid and its higher homologues and analogues.

After working with the salts of the isonitroso-oxazolones mentioned above, it was thought advisable to test the accuracy of the above hypothesis, from a different angle of view. If the intense colour of these compounds on salt formation with alkalies and organic bases be really due to the development of a true nitroso-(N = O) group in their molecular structure as the result of the transference of a labile hydrogen atom and production of a more acidic configuration, certainly the colour development will be much less, when there is a possibility of the formation of the same or more acidic configuration, but without the formation of the highly strained nitroso-group. And such a state of things becomes apparent when we take into consideration the salts of isonitroso-3-methyl-pyrazolone (VII) and isonitroso-3-phenyl-pyrazolone (VIII) :

Isonitroso-pyrazolones

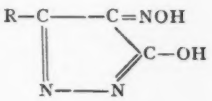


Oximino-ketonic forms



(IX) Nitroso-enolic forms

(VII) R = Me : Isonitroso-3-methyl-pyrazolone
(VIII) R = Ph : Isonitroso-3-phenyl-pyrazolone



(X) Oximino-enolic forms

The above weakly acidic oximino-ketonic structures of 3-substituted isonitroso-pyrazolones may undergo tautomerisation by transference of a hydrogen atom into two more highly acidic enolic forms in accordance with the scheme given above. It can be easily realised that when the comparatively much less strained and more acidic *oximino-enolic* form (X) is capable of existence, the highly strained and less acidic *nitroso-enolic* form (IX) will not be produced, and the colour of these compounds on salt formation will be much less intense than can be expected from a nitroso-enolic structure. From actual experimental evidence we find that the isonitroso-pyrazolones although so closely analogous to the corresponding isonitroso-isooxazolones in structure, yet from the point of view of colour, they are

much weaker, for, whereas the salts of isonitroso-isooxazolones are purple or deep magenta in colour with absorption maxima situated in the neighbourhood of 5800 Å, the salts of the corresponding isonitroso-pyrazolones are orange in shade with the absorption maxima in the neighbourhood of 4800 Å. It is perfectly apparent that the above theoretical exposition of the colour phenomenon of the salts of isonitroso-isooxazolones and isonitroso-pyrazolones is correct and this lends a further additional proof of the correctness of the "Theory of colour on the basis of molecular strain" advanced by Dutt.

The following ten salts of each of the four isonitroso-compounds mentioned above have been prepared and their absorption spectra determined in solution of aqueous acetone: potassium, sodium, ammonium, methylamine, ethylamine, dimethylamine, diethylamine, trimethylamine, *n*-butylamine and piperidine. All these salts are soluble in water with partial dissociation into constituents. In aqueous acetone (acetone containing about 5% of water) however such dissociation does not take place, and the colour of the salt is fully developed. In dry acetone as well as in other organic solvents, the colour is somewhat less intense, and the full intensity is only developed when a small quantity of water is added to the solution in those cases where the water is miscible with the solvents. The isonitroso-pyrazolones and isonitroso-isooxazolones possess remarkable power of crystallisation, and the same property is found transmitted in the salts also.

Experimental

Preparation of isonitroso-3-phenylisooxazolone.—

The method given in literature for the preparation of this compound (Claisen and Zedel[7]) being found to be very unsatisfactory both from the point of view of yield and purity, the following method was devised which gave a satisfactory yield of the pure material. The procedure adopted consists of two stags:—

(1) *Preparation of 3-phenyl-isooxazolone.*—Benzoyl-acetic ester (23 gm.) dissolved in glacial acetic acid (30 c.c.) was treated with hydroxylamine hydrochloride (8 gm.), and the mixture heated under reflux on the wire-gauze until the hydroxylamine hydrochloride completely dissolved and the product assumed a reddish brown colour. The excess of acetic acid was distilled off, and the residue (30 c.c.) allowed to cool, when it solidified completely to a mass of orange yellow crystals. These were washed with alcohol and recrystallised from boiling water, when the product was obtained in the form of pale cream coloured prismatic needles melting at 174° C. The yield was 18 gm.

(4) *Preparation of isonitroso-3-phenyl-isooxazolone.*—A mixture of 3-phenyl-isooxazolone (18 gm.) and sodium nitrite (10 gm.) dissolved in the minimum quantity of aqueous caustic soda (5%) was gradually treated with dilute sulphuric acid while being cooled under the tap, until the light buff-coloured precipitate of the isonitroso derivative was no longer formed. After standing overnight, the product was filtered off, washed with water, and recrystallised from boilling water in pale cream-coloured glistening rhombic prisms melting at 130° C. instead of 120° C. as found by previous workers (*cf.* Claisen and Zedel[7]). The yield was 18 gm.

The substance is soluble in all organic solvents and also in water to colourless or pale cream-coloured solutions. The aqueous, alcoholic or acetone solutions on dilution with water assume a pale pink coloration, thus recalling the behaviour of violuric acid. The substance is very souble in alkalies or organic bases with intense violet colorations.

Preparation of isonitroso-3-methylisooxazolone.—

The original method of preparation of this substance described in literature (Ceresole and Kockert[8] and also Nussberger[9]) being found to be very unsatisfactory due to an impure substance in a microscopic yield, the following new method was devised after a number of unsuccessful trials, which gave an excellent yield of the pure material. The procedure adopted consists of two stages, namely :

(1) *Preparation of isonitroso-acetoacetic ester.*—A mixture of finely powdered sodium nitrite (60 gm.) and acetoacetic ester (100 c.c.) was treated with dilute sulphuric acid (20%) with constant shaking and cooling with cold water, until a slight excess was added and there was no further effervescence. The mixture was allowed to stand overnight and the heavy layer of isonitroso-acetoacetic ester that had separated out was removed and dehydrated with calcium chloride. The yield was practically quantitative. The crude ester was directly converted into the next stage without any further purification.

(2) *Isonitroso-3-methyl-isooxazolone.*—A mixture of isonitroso-acetoacetic ester (120 gm.) and hydroxylamine hydrochloride (60 gm.) together with glacial acetic acid (30 c.c.) was heated on the water-bath until the hydroxylamine hydrochloride completely dissolved and there was no further evolution of hydrogen chloride (1½ hours). The product was diluted with water (30 c.c.) and repeatedly extracted with ether, until the last ethereal extract did not give any crimson coloration with dilute ammonia. The ethereal solution was washed with a little water, dried with calcium chloride and

the ether removed by distillation, when the isonitroso-compound was obtained in the form of a dark-red oil which quickly solidified to a mass of light brown crystals. The product was washed with benzene and recrystallised from pure ether with the addition of a little animal charcoal, when colourless feathery needles melting at 150° C. were obtained. The yield was 46 gm. The substance has got properties very similar to the corresponding phenyl derivative described before.

Preparation of isonitroso-3-phenyl-pyrazolone (Modified Method).—

(1) 3-*Phenyl-pyrazolone.*—This was obtained in good yield by treating benzoyl-acetic ester (28 gm.) with hydrazine hydrate (7 gm.) and alcohol (20 c.c.) and heating the mixture under reflux on a water-bath for ½ hour, when the pyrazolone crystallised out in fine colourless needles melting at 235° C. The yield was almost quantitative.

(2) The pyrazolone obtained above (20 gm.) was ground up with water (200 c.c.) to a fine paste or emulsion, and nitrous anhydride generated from sodium nitrite and dilute sulphuric acid was passed in until the whole mass was saturated and the substance turned orange yellow. The product was filtered off and recrystallised from boiling water in fine glistening orange hexagonal prisms melting at 188° C. Yield was almost quantitative (22 gm. *Cf.* Rothenburg[10]).

Preparation of isonitroso-3-methyl-pyrazolone.—

This was obtained by a modification of the original method described in literature by Curtius,[11] according to the scheme given above in the case of the corresponding phenyl compound, the essential difference between the two being that instead of benzoyl-acetic ester, acetoacetic ester was used. The substance crystallises from boiling water in bright yellow glistening hexagonal prisms melting at 217° C. instead of 130° C. as given by Curtius. The yield obtained was about 85% of the theoretical.

Preparation of salts.—

The isonitroso-pyrazolones and -oxazolones described above were converted into salts by treating the substances dissolved in acetone with a slight excess of the organic and inorganic bases, when in most instances the salt crystallised out from the solution almost immediately in fine glistening crystals. Where however such crystallisation did not occur, the acetone solution of the salt was quickly evaporated at the ordinary temperature with the help of a blast from an electric table fan, when the salt invariably came out in fine form. After washing with ether in order to remove the excess of the base, the product was obtained perfectly pure.

The salts prepared in this way are beautifully crystalline compounds the description and properties of which have been given in tabular forms at the end of the paper. All these susbstances are very soluble in alcohol, acetone and water, moderately soluble in chloroform and insoluble in ether, benzene and petroleum ether. The absorption maxima of these compounds have been determined in aqueous acetone solution with the help of a Hilger constant deviation glass spectrograph, the results being incorporated in the tables mentioned above.

Summary and Conclusions

(1) Like violuric acid and diphenyl-violuric acid, isonitroso-3-methyl-isooxazolone and isonitroso-3-phenyl-isooxazolone have been found to form very intense, *i.e.*, purple and magenta coloured salts with organic and inorganic bases, while the substances themselves are almost colourless and dissolve in water and organic solvents to colourless solutions.

(2) This behaviour of the above-mentioned compounds on salt formation has been shown to be due to a fundamental change in the constitution of the molecules from oximino-ketonic to nitroso-enolic forms with consequent changes in the molecular strain and therefore the absorption of these substances.

(3) The change of colour of these substances from colourless to purple or magenta is sufficiently sharp and intense for them to act as excellent indicators.

(4) The validity of the hypothesis with regard to the colour phenomena of the above-mentioned isonitroso-iso-oxazolones is borne out by taking into consideration the organic and inorganic salts of isonitroso-3-methyl-pyrazolone and isonitroso-3-phenyl-pyrazolone. In these substances there is an alternative more acidic but less strained oximino-enolic configuration possible of existence, and consequently the salts of these isonitroso-pyrazolones have less strained structures and their colours also are far less intense than the corresponding salts of the isonitroso-isooxazolones mentioned before, in spite of all of them possessing very closely analogous molecular structures. The behaviour of all these substances therefore lends a further additional proof to the correctness of the " Theory of colour on the basis of molecular strain " advanced by Dutt.

TABLE I. *Salts of isonitroso-3-phenyl-isooxazolone*

Salt with	Colour in solid state	Remarks	M.P. (Decom.) °C.	Colour in solution	Absorption maxima (Å)	Analysis % N. (Theoretical within bracket)
Methylamine ..	Orange	Glistening rectangular plates	122	Violet	5790	19·20 (19·00)
Ethylamine ..	Deep pink	Glistening rhombic plates	112	Do.	5750	18·20 (17·8)
Dimethylamine ..	Orange-red	Do.	102	Do.	5750	18·10 (17·8)
Diethylamine ..	Do.	Glistening cubical crystals	103	Do.	5690	17·50 (17·0)
Trimethylamine	Yellow	Rectangular prisms	110	Do.	5600	18·20 (18·0)
n-Butylamine ..	Red	Glistening rhombic plates	82	Do.	5730	17·30 (17·0)
Piperidine ..	Crimson	Do.	121	Do.	5620	14·60 (15·2)
Sodium ..	Deep pink	Glistening rectangular prisms	110	Do.	5850	13·60 (13·2)
Potassium ..	Yellow	Glistening needles	122	Bluish-violet	5910	12·07 (12·2)
Ammonium ..	Mauve	Rectangular prisms	86	Violet	5810	19·90 (20·3)
Free acid	Pale cream	Rhombic prisms with silky lustre	130	Pale pink	5300	14·84 (14·7)

TABLE II. *Salts of isonitroso-3-methyl-isooxazolone*

Salt with	Colour in solid state	Remarks	M.P. (Decom.) °C.	Colour in solution	Absorption maxima (Å)	Analysis % N. (Theoretical within bracket)
Methylamine ..	Chocolate-brown	Rectangular plates	107	Deep magenta	5760	26·4 (26·4)
Ethylamine ..	Biscuit	Rectangular prisms	108	Do.	5555	24·7 (24·2)
Dimethylamine ..	Orange	Rectangular plates	102	Do.	5485	24·6 (24·2)
Diethylamine ..	Brownish-orange	Glistening rhombic plates	87	Do.	5430	21·3 (20·8)
Trimethylamine	Orange-brown	Rectangular plates	72	Do.	5350	22·8 (22·4)
n-Butylamine ..	Cream	Cubical crystals	112	Do.	5370	21·4 (20·8)
Piperidine ..	Orange	Rectangular plates	..	Do.	5335	20·1 (19·7)
Sodium ..	Creamy yellow	Rectangular prisms	210	Deep carmine	5860	19·0 (18·6)
Potassium ..	Brownish-yellow	Prismatic needles and plates	..	Do.	5890	16·9 (16·8)
Ammonium ..	Salmon	Rhombic plates	96	Deep magneta	5770	29·4 (28·9)
Free acid ..	Pale cream	Glistening feathery needles	150	Pale pink	5300	21·9 (21·8)

TABLE III. *Salts of isonitroso-3-phenyl-pyrazolone*

Salt with	Colour in solid state	Remarks	M.P. (Decom.) ° C.	Colour in solution	Absorption maxima (Å)	Analysis % N. (Theoretical within bracket)
Methylamine ..	Brownish red	Glistening rectangular plates	155	Yellow-brown	4928	25·6 (25·4)
Ethylamine ..	Do.	Do.	170	Orange	4960	24·4 (23·9)
Dimethylamine ..	Orange-yellow	Glistening rhombic plates	185	Orange-brown	4850	23·4 (23·9)
Diethylamine ..	Do.	Do.	193	Brown-yellow	4865	21·8 (21·3)
Trimethylamine	Do.	Do.	185	Do.	4935	22·1 (22·5)
n-Butylamine ..	Do.	Do.	176	Do.	4815	21·2 (21·3)
Piperidine ..	Do.	Do.	211	Do.	4715	20·8 (20·4)
Sodium ..	Brownish-orange	Do.	..	Reddish-brown	4950	19·9 (19·7)
Potassium ..	Orange-brown	Do.	239	Do.	5045	17·3 (17·0)
Ammonium ..	Brick-red	Glistening rhombic prisms	184	Do.	4995	26·8 (27·1)
Free acid ..	Orange	Glistening rectangular and rhombic prisms	188	Orange	4650	22·4 (22·2)

TABLE IV. *Salts of isonitroso-3-methyl-pyrazolone*

Salt with	Colour in solid state	Remarks	M.P. (Decom.) ° C.	Colour in solution	Absorption maxima (Å)	Analysis % N. (Theoretical within bracket)
Methylamine ..	Chocolate-brown	Cubical crystals	167	Orange-red	4932	35·7 (35·4)
Ethylamine ..	Reddish-brown	Glistening rectangular plates	135	Do.	4780	32·9 (32·5)
Dimethylamine ..	Brownish-yellow	Rectangular prisms	161	Do.	4770	32·7 (32·5)
Diethylamine ..	Orange-red	Cubical crystals	173	Do.	4770	28·4 (28·0)
Trimethylamine	Brownish-yellow	Rectangular prisms	169	Do.	4755	20·5 (30·1)
n-Butylamine ..	Carmine-red	Glistening rectangular prisms	134	Do.	4770	28·5 (28·0)
Piperidine ..	Orange-yellow	Rhombic plates	158	Do.	4750	26·8 (26·4)
Sodium ..	Turmeric-yellow	Prismatic needles	..	Brownish-red	5080	28·4 (28·18)
Potassium ..	Deep salmon	Rectangular plates	273	Crimson	5180	25·7 (25·4)
Ammonium ..	Orange-yellow	Glistening rectangular prisms	214	Orange-red	4810	39·2 (38·88)
Free acid ..	Yellow	Glistening hexagonal prisms	217	Yellow	4470	33·4 (33·0)

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